TRANSITION METAL–CARBENE COMPLEXES

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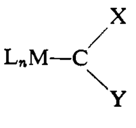
Contents

I. Introduction

The term metal–carbene complexes refers here to compounds of the general type



in which a carbene, :CXY, is coordinated to a metal atom, M, and L_n simply represents the various other coordinated ligands. At the present time, few complexes [which are of Hg(II), Pt(II), and Pd(II), and a Cr(0) complex; see Table III] are known which have more than one carbene ligand per metal center. The carbene *ligand* is usually bound terminally, but is also found as a bridging moiety. In the latter case, the "carbene-carbon" atom, C_{carb}, is no longer trigonal, and such compounds do not come within the scope of this review, although brief reference is made to a few examples. However, the complex $(Me_3SiCH_2)_2Nb(CSiMe_3)_2Nb(CH_2SiMe_3)_2$ might be regarded as having bridging (metallo)carbene groups.[1] Complexes are usually neutral, but cationic species are also known and anionic ones have been postulated as reaction intermediates (see section VI). For cationic and anionic complexes, an alternative symbolism is to regard these compounds as transition metal substituted carbonium ions or carbanions. Likewise neutral carbene complexes may be alternatively regarded as transition metal ylides, like the Wittig (*e.g.*, Ph_3PCH_2) and related reagents.[1a] The carbene may be considered a "soft" ligand, being normally found in complexes in which the metal is in a low oxidation state, but Rh(III) and Pt(IV) compounds have been described; the carbene ligand for our purpose is classed as a neutral species. With a very few exceptions (see section III.F), stable carbene complexes have been prepared only when either X or Y (or both) is an element other than carbon (a heteroatom), commonly O, S, or N; and π interaction between the carbene carbon (C_{carb}) and X or Y is an important factor in stabilizing the complexes. The free carbene :CXY is thus classified as a nucleophilic carbene. As will be seen, C_{carb} may be regarded in valence-bond language as an sp^2 C. However, the term carbene complex does not include alkenyl- or alkynyl-metal compounds and related species, in which a carbon ligand atom is formally doubly bonded to X or Y.

Although the first carbene complexes were evidently prepared in 1915,[1b] they were not recognized as such until recently,[2,3] and the current interest started with the preparation of $(OC)_5WC(OMe)Ph$,[4] the first carbene complex to be so

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(1) F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1477 (1971).

(1a) But with opposite polarity.

(1b) L. Chugaev and M. Skanavy-Grigorizeva, *J. Russ. Chem. Soc.*, 47, 776 (1915).

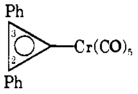
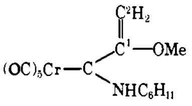
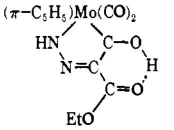
(2) G. Rouschias and B. L. Shaw, *Chem. Commun.*, 183 (1970).

(3) A. Burke, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 92, 2555 (1970); W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 10, 2416 (1971).

(4) E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, 3, 580 (1964).

Table I

X-Ray Structural Data for Carbene Complexes of Cr, Mo, and W[a]

Complex	*Molecular parameters*		*Remarks*	*Ref*
$(OC)_5CrC(OMe)Ph$	$M\text{-}C_{carb}$	2.04	Cr pseudooctahedral, phenyl group at 90° to plane of sp^2 C_{carb}; (O)Me group is cis to Cr	6
	$C_{carb}\text{-}O$	1.33		
	O-Me	1.46		
	$C_{carb}\text{-}Ph$	1.47		
	M-CO(*trans*)	1.87		
	M-CO(*cis*)	1.86-1.91		
$(OC)_5WC(OMe)Ph$	Similar to Cr analog			6
$(Ph_3P)(OC)_4CrC(OMe)Me$	$M\text{-}C_{carb}$	2.00	Essentially octahedral Cr, with cis arrangement of substituents; the (O)Me group now trans to Cr	7
	$C_{carb}\text{-}O$	1.32		
	O-Me	1.49		
	Cr-P	2.42		
$(OC)_5CrC(NHMe)Me$	$M\text{-}C_{carb}$	2.09	Essentially octahedral Cr, (N)Me group trans to Cr	11
	$C_{carb}\text{-}N$	1.33		
	N-Me	1.51		
	$C_{carb}\text{-}Me$	1.51		
$(OC)_5CrC(NEt_2)Me$	$M\text{-}C_{carb}$	2.16	Metal pseudooctahedral	8
	$C_{carb}\text{-}N$	1.31		
	$N\text{-}CH_2$	1.50		
	$C_{carb}\text{-}Me$	1.50		
	$M\text{-}C_{carb}$	2.05	Cr approximately octahedral; distortion of ring toward cyclopropene	21
	C-Ph (both)	1.45		
	M-CO	1.88-1.92		
	C^3C^2	1.35		
	$M\text{-}C_{carb}$	2.15	Cr approximately octahedral; first known carbene complex with exact mirror symmetry (*Pnma*) (point group C_s); Me group cis to vinyl ether, cyclohexyl ring in chair conformation	25
	$C_{carb}\text{-}N$	1.32		
	$C^1\text{-}C^2$	1.33		
	$C^1\text{-}O$	1.36		
	$O\text{-}CH_3$	1.42		
	$M\text{-}C_{carb}$	2.09	But see Addendum, Table X, for revised structure	24
	M-N	2.11		

[a] Bond lengths are reported in Å (errors not reported).

formulated. A brief summary, mainly of work with stable carbene complexes of Cr, Mo, and W, carried out by Fischer and coworkers, has recently appeared.[5]

In the present review, our main aim has been to provide a comprehensive account to Nov 1971, relating to syntheses and properties of stable carbene complexes. Additionally, selected data on metal-carbene intermediates are presented in section VI, but a comprehensive account is available; see section VI.

II. Structure and Bonding

Structural data for carbene complexes are summarized in Tables I and II. For the compounds of the group VI metals (Table I), C_{carb} and the three substituents M, X, and Y are coplanar, and the bond angles about C_{carb} [*e.g.*, 122, 104, and 134° for $(CO)_5CrC(OMe)Ph$[6]] clearly show the sp^2 character of the carbon. This description receives support from the C_{carb}-X bond lengths; *e.g.* (X = O), 1.33 Å in the same complex is considerably shorter than a normal C-O single bond distance (~1.43 Å) and is even shorter than corresponding C-O bonds in esters. This implies p_π-p_π overlap, involving the empty p orbital of the C_{carb}. The phenyl substituent of this compound lies approximately perpendicular to the C_{carb} bonding plane and presumably there is no π overlap with the aromatic system. However, the C_{carb}-Ph bond length, 1.47 Å, is fully consistent with a bond between two trigonal carbons. The bonding in these complexes may be described in terms of the donation of a pair of electrons from an sp^2 set of the (singlet) carbene-carbon atom to the metal, and back-donation of electrons from the metal into the vacant (p_z) orbital on C_{carb}; the relative weights of these is discussed below. The metal-carbon distance (2.04 Å) is significantly longer than the Cr-C(O) distances (1.96-1.91 Å). A similar lengthening is found also in the complex *cis*-triphenylphosphine(methoxymethylcarbene)tetracarbonylchromium(0)[7] and in related complexes, and is not therefore due to the steric influence of the phenyl group. A more probable reason, receiving much confirmatory evidence from spectroscopic data, is that the π-acceptor/σ-donor ratio is significantly lower for carbene ligands than for CO. This view is in harmony with the observation

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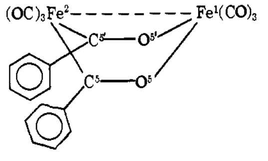
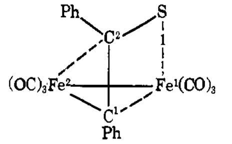
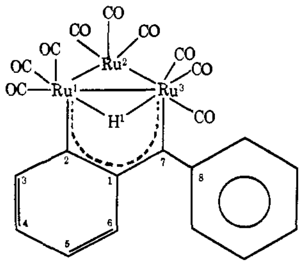
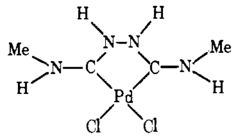
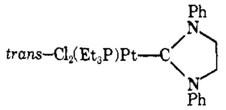
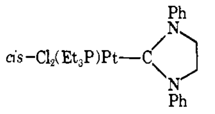
(5) E. O. Fischer, *Rev. Pure Appl. Chem.*, 24, 407 (1970).

(6) O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 642 (1968).

(7) O. S. Mills and A. D. Redhouse, *ibid.*, 1274 (1969).

Table II

X-Ray Structural Data for Carbene Complexes of Groups VII and VIII Metals

Complex	*Molecular parameters*		*Remarks*	*Ref*
$NMe_4{}^+[(\pi\text{-}C_5H_5)(OC)_2MnC(O)Ph]^-$	Mn–C_{carb} C_{carb}–O C_{carb}–Ph Mn–C(O)	1.95 1.28 1.49 1.78, 1.77	The cyclopentadienyl ring is π-bonded and essentially planar	18
	Fe^2–$C^{5,5'}$ C^5–O^5 Fe^1–O^5 Fe^1–Fe^2 $\angle Fe^2C^5O_5$ $\angle C^5Fe^2C^{5'}$	1.945 1.262 1.967 2.568 114.6° 84.1°	Both metals have distorted octahedral environment and lie in a crystallographic mirror plane	17
	Fe^2–C^2 Fe^1–C^1 Fe^2–C^1 Fe^1–S Fe^1–Fe^2	2.654 2.089 1.969 2.243 2.533		19
	Av Ru–C_{carb} Av Ru–C(O)	2.09 1.91	Ru_1 Ru_3 C_1–C_2–C_7 all coplanar Ring 1–6 shows marked bond-length alternation; phenyl ring at 90° to plane	20
	Pd–C_{carb} C_{carb}–N_{ex} C_{carb}–N_{ring} N–N Pd–Cl	1.948 1.327 1.309 1.395 2.387	N and C not distinguished, but molecular geometry established; molecule C_{2v}	3
cis-$Cl_2(Et_3P)PtC(OEt)NHPh$	Pt–C_{carb} C_{carb}–O C_{carb}–N Pt–P Pt–Cl	1.98 1.32 1.33 2.24 2.365, 2.368	Square-planar platinum; C_{carb} environment planar (2 planes approximately perpendicular)	14
	Pt–C_{carb} C_{carb}–N Pt–P Pt–Cl N–C(Ph) N–C(sp^3)	2.02 1.35 2.29 2.31 1.40 1.49	Square-planar platinum; C_{carb} environment planar; 2 planes at 70.7° (the planes are coplanar to 0.020 and 0.006 Å, respectively)	12
	Pt–C_{carb} C_{carb}–N Pt–Cl(trans to Cl) Pt–Cl(trans to carb) Pt–P N–C(Ph) N–C(sp^3)	2.01 1.33 2.38 2.36 2.23 1.40 1.48	Square-planar platinum; C_{carb} environment planar	26

that much of the electrophilicity of C_{carb} is relieved by p_π–p_π bonding with oxygen. Replacement of the heteroatom oxygen by nitrogen in the complex $(OC)_5CrC(NEt_2)Me$ results in a yet longer Cr–C_{carb} distance (2.16 Å).[8] In this case, the bond can have little double bond character, since the calculated Cr–C(sp^2) single bond distance is 2.21 Å [using a covalent radius for Cr(0) of 1.48 Å[9]]. As would be expected, the C_{carb}–N distance is short, 1.31 Å, comparable with the corresponding distance in acetanilide (1.35 Å).[10] The Cr–C(O) distances

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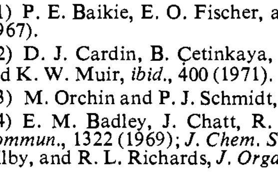
(8) J. A. Connor and O. S. Mills, *J. Chem. Soc. A*, 334 (1969).

(9) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

trans to the carbene group are shorter than other metal carbonyl bonds in the complexes $(OC)_5CrC(OMe)Ph$,[6] $(OC)_5CrC(OMe)Me$,[6] $(OC)_5CrC(NHMe)Me$,[11] and $(OC)_5CrC(NEt_2)Me$[8] [and shorter than others apart from that trans to phosphine in $(Ph_3P)(OC)_4CrC(OMe)Me$[7]]. While individual differences are not always experimentally significant, together they certainly suggest that back-donation from Cr to C(O) is enhanced by the presence of a trans carbene group, which thus competes unequally for formally nonbonding electrons localized on Cr.

Turning to the platinum–carbene complexes for which structural data are available (Table II), similarities are evident. For example, the bonding environment of C_{carb} is again trigonal, Pt–C_{carb} is longer than other platinum(II)–carbon distances [*e.g.*, Pt–C(O)], and there is considerable shortening of the C–X and/or C–Y bonds. In the compound *trans*-$Cl_2(PEt_3)PtC(NPhCH_2)_2$, the atoms forming the C_{carb} environment are coplanar to within 0.006 Å.[12] The Pt–C_{carb} distance (2.02 Å) is significantly longer than the platinum–carbon distance[13] (1.74 Å) in *trans*-$[Cl_2(4\text{-}MeOC_6H_4NO)PtCO]$ and other carbonyl derivatives, and the C_{carb}–N lengths (1.35 Å) are likewise shorter than expected for single bonds. In this case, as in *cis*-$Cl_2(PEt_3)PtC(OEt)NHPh$,[14] π-bonding appears to lie predominantly within the CXY moiety rather than in the Pt–C bond. The platinum–carbon distance of the imidazolidinylidene complex is very close[12] to the predicted[15] single bond length (2.05 Å). It is interesting to note that in both the cis and trans platinum derivatives, bond lengths trans to the carbene (Pt–Cl 2.365[14] and Pt–P 2.29 Å,[12] respectively) show a trans influence for that ligand very close to that of a tertiary phosphine (see section V). Similar conclusions may be made on the basis of (i) the Pt–Cl bond length in cis complexes [which are almost identical with those found in *cis*-$(R_3P)_2Cl_2Pt$], and (ii) spectroscopic data (see section V). In the infrared (ir) spectrum of the cis carbene,[14] there is a band at 3130 cm^{-1} (which moves to 2240 cm^{-1} on deuteration) corresponding to a N–H stretching mode.[14] This is some 200–300 cm^{-1} lower than found[16] in the chromium carbene complexes $(OC)_5CrC(RHN)Me$ and possibly implies a partial positive charge on the XY (O, N) atoms, the greater part being at the less electronegative nitrogen center. This suggests a contribution to the structure of the ylide forms **1** and **2**, with **1** being the more important.

The structure of $(OC)_3Fe(PhC\text{-}O)_2Fe(CO)_3$ once again reveals a planar environment for the C_{carb} atoms (in this case within 0.001 Å) and a much shortened (1.26 Å) C_{carb}–O bond.[17] These features would also be expected for a benzoyl complex, but clearly no decision between the two formulations can be made from these data, although the previous shortest C_{carb}–O length (1.30 Å) occurs in the anion $[\pi\text{-}C_5H_5(OC)_2MnC(O)Ph]^-$.[18] As in carbene complexes, the M–C_{carb} distance (1.95 Å) is markedly longer than the metal-carbonyl lengths (1.80 Å) indicating much lower π character. The phenyl group is also twisted from the plane of the carbene ligand and is presumably not involved in π overlap with C_{carb}.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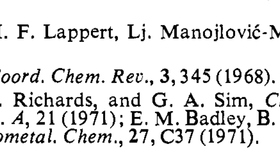
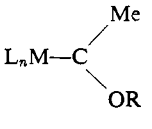

2

The complex $(OC)_3Fe[PhC.C(Ph)S]Fe(CO)_3$ presents rather a different picture.[19] It is difficult to make valid comparisons (*e.g.*, the uncertainty in the radius of Fe) in a structure of this type, but the spatial arrangement (see Table II) indicates that a delocalized π system predominates in the bonding of the "carbene ligand." It is probably better to regard this as a complex formed from reaction of the intermediate carbene with an iron substrate rather than as a "carbene complex."

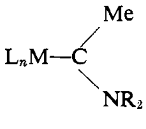
The carbene in $Ru_3(CO)_9H[C(C_6H_5)C_6H_4]$ is also bonded in a most unusual way, there being interactions with all three ruthenium atoms.[20] The mean Ru–C_{carb} distance is not very much greater than the mean ruthenium-carbonyl distance, suggesting a significant amount of double bonding with the metal. This is supported by the coplanarity of the three-carbon framework of the carbene ligand and the two metal atoms to which it is bonded (see Table II). Once again, a delocalized π system is an apposite description. The first compound reported without a stabilizing heteroatom present in the carbene ligand, pentacarbonyl(2,3-diphenylcyclopropenylidene)chromium(0), presents a somewhat similar situation.[21] There is considerable double bond character in the metal–carbene bond (2.05 Å) (*e.g.*, see ref 7) and a distortion of the three-membered ring toward a cyclopropene system. The carbon–carbon distances of the ring are not, however, very different from those of the aromatic triphenylcyclopropenylium cation,[22] and the stability of the complex is undoubtedly associated with aromaticity in the carbene ligand.

The X-ray analysis of *cis*-$Cl_2PdC(NMeH)NHNHCNMeH$ (see Table III), a palladium analog of the "Chugaev-salt" type[3] establishes the dicarbene type of structure first put forward[2] on the basis of nmr studies for these complexes.

In summary, for simple group VI carbene complexes there are structural resemblances between alkoxycarbene- and aminocarbene-metal complexes, such as


$L_nM\text{—}C(Me)(OR)$

and


$L_nM\text{—}C(Me)(NR_2)$

and carboxylic esters and amides, respectively. Thus, the C_{carb}–O and C_{carb}–N bonds have considerable multiple bond character, as indicated by their lengths, and also by the high energy barriers to rotation about C–O and C–N bonds,

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(10) C. J. Brown, *Acta Crystallogr.*, **21**, 442 (1966).

(11) P. E. Baikie, E. O. Fischer, and O. S. Mills, *Chem. Commun.*, 1199 (1967).

(12) D. J. Cardin, B. Çetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *ibid.*, 400 (1971).

(13) M. Orchin and P. J. Schmidt, *Coord. Chem. Rev.*, **3**, 345 (1968).

(14) E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1322 (1969); *J. Chem. Soc. A*, 21 (1971); E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Organometal. Chem.*, **27**, C37 (1971).

(15) *Chem. Soc. Spec. Publ.*, No. **18** (1965).

(16) J. A. Connor and E. O. Fischer, *J. Chem. Soc. A*, 578 (1969).

(17) P. F. Lindley and O. S. Mills, *ibid.*, 1279 (1969); E. O. Fischer, V. Kiener, D. St. P. Bunbury, E. Frank, P. F. Lindley, and O. S. Mills, *Chem. Commun.*, 1378 (1968); E. Frank and D. St. P. Bunbury, *J. Chem. Soc. A*, 2143 (1970).

(18) E. Hädicke and W. Hoppe, *Acta Crystallogr., Sect. B*, **27**, 760 (1971).

(19) G. N. Schrauzer, H. N. Rabinowitz, J. A. K. Frank, and I. C. Paul, *J. Amer. Chem. Soc.*, **92**, 212 (1970).

(20) A. W. Parkins, E. O. Fischer, G. Huttner, and D. Regler, *Angew. Chem., Int. Ed. Engl.*, **9**, 633 (1970).

(21) G. Huttner, S. Schelle, and O. S. Mills, *ibid.*, **8**, 515 (1969).

(22) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

whereas the barriers to rotation about the metal-C bonds are not high (see section V). Furthermore, C_{carb} has electrophilic character, as is evident from the highly deshielded C_{carb} (^{13}C nmr spectrum; see section V),[23] and the OR displacement reactions (*e.g.*, by NR_2; see sections III.C and IV.B.1). The latter reactions, incidentally, support the suggestion (see above) that $\overset{\curvearrowright}{O}—C_{carb}$ is less significant than $\overset{\curvearrowright}{N}—C_{carb}$; and finally the hydrogen atoms of CH_3-C_{carb} have considerable acidity (see section III.C). It is generally considered that a nucleophilic carbene ligand is a strong σ donor but a poor π acceptor, and spectroscopic and electric dipole moment data (see section V), as well as the results discussed above, have been cited in support.

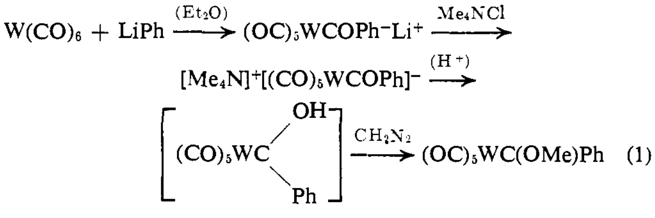
III. Syntheses

A. INTRODUCTION

In the brief time since the first authenticated report of a carbene complex by Fischer and Maasböl,[4] several methods of preparation have been discovered. The various types of synthesis have differed widely in generality and it will be convenient to deal with each separately. They may be classified according to the headings of sections III.B to III.J. In Table III data are collected for transition metal-carbene complexes, including methods of synthesis.

B. SYNTHESES INVOLVING MODIFICATION OF A COORDINATED (NONCARBENE) CARBON LIGAND

The early syntheses of group VI metal-carbene complexes involved attack at coordinated carbonyl by nucleophiles (LiMe, LiPh, etc.) to give the anionic acyllithium salts which could be converted into the corresponding tetraalkylammonium compounds. Acidification followed by treatment with diazomethane afforded the carbene complexes. This is illustrated in eq 1. The yields are generally good except for the last two stages where they are variable [*e.g.*, $(OC)_5WC(OMe)Ph$, 31%; $(OC)_5WC(OMe)Me$, 77%; based on the ammonium salts].[27]



$$W(CO)_6 + LiPh \xrightarrow{(Et_2O)} (OC)_5WCOPh^-Li^+ \xrightarrow{Me_4NCl} [Me_4N]^+[(CO)_5WCOPh]^- \xrightarrow{(H^+)} \left[(CO)_5WC\begin{smallmatrix}OH\\ \\Ph\end{smallmatrix}\right] \xrightarrow{CH_2N_2} (OC)_5WC(OMe)Ph \quad (1)$$

not isolated

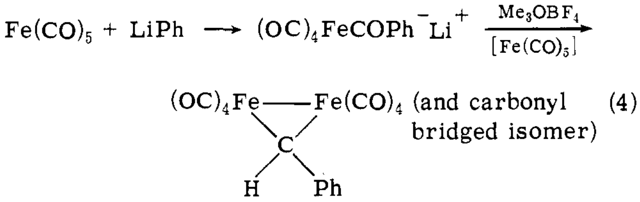
The hydroxycarbene–group VI metal intermediates were not isolated (for Fe, Ru, and Re compounds, see Table III), and attempts to do so by removal of solvent from solutions afforded aldehyde (acetaldehyde and benzaldehyde from methoxy- and phenoxycarbenes, respectively) and metal hexacarbonyl.[25] This behavior is similar to that found upon addition of excess aryllithium reagents to iron pentacarbonyl, followed by acidification, when the aromatic aldehyde was formed in 60% yield together with small quantities of other aromatic carbonyl compounds.[28]

It was later discovered that oxonium salts are good alkylating agents in this synthesis, and furthermore can be used directly on the lithium salts, as illustrated in eq 2.[29a,b]

$$Cr(CO)_6 + LiMe \xrightarrow{(Et_2O)} (OC)_5CrCOMe^-Li^+ \xrightarrow[(H_2O)]{Me_3OBF_4} (OC)_5CrC(OMe)Me + LiBF_4 + Me_2O \quad (2)$$

The great generality and usefulness of this method is readily appreciated from a glance at the appropriate column of Table III; only a few examples will be discussed here. The lithium salts react with chlorotrimethylsilane directly at ambient temperatures affording siloxycarbenes (eq 3).[30] The process is not always straightforward; for example, with iron pentacarbonyl the reaction takes an unexpected course (eq 4).[31] The anion $(OC)_nMCOR^-$ may clearly behave either as an alkoxy anion (*e.g.*, eq 3) or as a carbanion (*e.g.*, eq 4).

$$(OC)_5CrCOMe^-Li^+ + ClSiMe_3 \longrightarrow (OC)_5CrC(OSiMe_3)Me + LiCl \quad (3)$$



$$Fe(CO)_5 + LiPh \longrightarrow (OC)_4FeCOPh^-Li^+ \xrightarrow[{[Fe(CO)_5]}]{Me_3OBF_4} (OC)_4Fe—Fe(CO)_4 \text{ (and carbonyl bridged isomer)} \quad (4)$$

It is also interesting that reaction of the lithium ferrate $(OC)_4FeCOPh^-Li^+$ with trityl chloride results in oxidation[31] and formation of the di-μ-acyl-diiron hexacarbonyls. The structures of these are known[17] to involve bonding of both carbene carbon atoms to the same metal atom, and this reaction must therefore involve molecular rearrangement. The formation of the μ-hydrido-carbonyl cluster carbene complex[20] $Ru_3(CO)_9H(C_6H_5CC_6H_4)$ presumably follows a different course, but again the oxygen atom of the reactive carbonyl group is lost. However, it is not only mononuclear carbonyls which behave in the simplest fashion, as illustrated in eq 5.[32]

$$Mn_2(CO)_{10} + LiR \longrightarrow (OC)_9Mn_2COR^-Li^+ \xrightarrow{R^1_3OBF_4} (OC)_9Mn_2C(OR^1)R \quad (5)$$

This synthesis is not restricted to alkyl- and aryllithiums. Ferrocenyllithium[33] reacts with chromium hexacarbonyl, and treatment with Et_3OBF_4 affords complex **3**. Alkoxyaminocarbene complexes can be prepared directly using dialkylamidolithium reagents (eq 6).[34]

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(23) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).

(24) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1952 (1969).

(25) G. Huttner and S. Lange, *Chem. Ber.*, **103**, 3149 (1970).

(26) D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, Lj. M. Muir, and K. W. Muir, *J. Organometal. Chem.*, in press.

(27) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967).

(27a) C. G. Kreiter and E. O. Fischer, *ibid.*, **103**, 1561 (1970).

(28) M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 341 (1964).

(29) (a) R. Aumann and E. O. Fischer, *Chem. Ber.*, **101**, 954 (1968); (b) M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, **9**, 32 (1970); (c) *Inorg. Chim. Acta*, **5**, 247 (1971).

(30) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **12**, P1 (1968).

(31) E. O. Fischer and V. Kiener, *ibid.*, **23**, 215 (1970).

(32) E. O. Fischer and E. Offhaus, *Chem. Ber.*, **102**, 2449 (1969).

(33) G. A. Moser, E. O. Fischer, and M. D. Rausch, *J. Organometal. Chem.*, **27**, 379 (1971); J. A. Connor, E. M. Jones, and J. P. Lloyd, *ibid.*, **24**, C20 (1970).

(34) E. O. Fischer and H. J. Kollmeier, *Angew. Chem., Int. Ed. Engl.*, **9**, 309 (1970).

Table III

Syntheses and Chemical and Physical Properties of Carbene Complexes[a]

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
		Chromium Compounds (Oxycarbene Ligands)		
$(OC)_5CrC(OMe)Me$	34	B $(60)^{27}$ $(87)^{29a}$	X-Ray, Table I; ν(CO) (Nujol) 2070s, 1992s, 1953vs; nmr; y n	27, 29a
$(CO)_5CrC(OMe)Et$		C (100?)	Prepared in soln using base-catalyzed H exchange	36, 37
$(OC)_5CrC(OMe)Pr^i$		C (100?)	Prepared in soln using base-catalyzed H exchange	36, 37
$(OC)_5CrC(OMe)Ph$	46	B (55)	X-Ray, Table I; ν(CO) (Nujol) 2066s, 1992s, 1953vs; o c	27, 38
$(OC)_5CrC(OMe)C_6H_4NMe_2$-*p*	131 (dec)	B (55)	ν(CO) 2054m, 1976w, 1943s, 1935vs (hexane); r n	38
$(OC)_5CrC(OMe)C_6H_4OMe$-*p*	103	B (45)	ν(CO) 2058m, 1981w, 1954s, 1941vs (hexane); br c	38
$(OC)_5CrC(OMe)C_6H_5Me$-*p*	71	B (78)	ν(CO) 2061m, 1985w, 1959s, 1950vs, 1939sh (hexane); d-r c	38
$(OC)_5CrC(OMe)C_6H_4F$-*p*	64	B (63)	ν(CO) 2062m, 1986w, 1963s, 1951vs, 1942sh (hexane); d-r c	38
$(OC)_5CrC(OMe)C_6H_4Cl$-*p*	107	B (53)	ν(CO) 2063m, 1986w, 1964s, 1952vs, 1944sh (hexane); d-r c	38
$(OC)_5CrC(OMe)C_6H_4Br$-*p*	109	B (42)	ν(CO) 2063m, 1987w, 1965s, 1953vs, 1944sh (hexane); d-r c	38
$(CC)_5CrC(OMe)C_6H_4CF_3$-*p*	102	B (64)	ν(CO) 2065m, 1990w, 1971s, 1955vs, 1948sh (hexane); r c	38
$(OC)_5CrC(OMe)C_6H_4NMe_2$-*m*	43	B (62)	ν(CO) 2060m, 1984w, 1956s, 1948vs (hexane); r c	38
$(OC)_5CrC(OMe)C_6H_4Cl$-*m*	49	B (40)	ν(CO) 2064m, 1988w, 1968s, 1954vs, 1945sh (hexane); r c	38
$(OC)_5CrC(OMe)C_6H_4CF_3$-*m*	45	B (56)	ν(CO) 2064m, 1989w, 1969s, 1955vs, 1946sh (hexane); l-r c	38
$(OC)_5CrC(OMe)C_6H_4OMe$-*m*	(Oil)	B (35)	ν(CO) 2063m, 1987w, 1964s, 1952vs, 1944sh (hexane); d-r	38
$(OC)_6CrC(OMe)C_6H_4OMe$-*o*	73	B (38)	ν(CO) 2062m, 1987w, 1948s, 1954vs (hexane); l-r c	38
$(OC)_5CrC(OMe)C_6H_4CF_3$-*o*	56	B (42)	ν(CO) 2069m, 1994w, 1969s, 1956vs (hexane); l-r c	38
$(OC)_5CrC(OMe)$-2,4,6-$C_6H_2Me_3$	84	B (67)	ν(CO) 2065m, 1989w, 1952vs (hexane); o-r	38
$(OC)_5CrC(OMe)$-2,6-$C_6H_3(OMe)_2$	116	B (51)	ν(CO) 2062m, 1985w, 1940s, 1954vs (hexane); o-y c	38
$(OC)_5CrC(OMe)$-1-naphthyl	90	B (66)	ν(CO) 2066m, 1990w, 1964s, 1954vs (hexane); r c	38
$(OC)_5CrC(OMe)CH_2Ph$	39	B (46)	ν(CO) 2063m, 1962s, 1946vs (hexane); y n	38
$(OC)_5CrC(OEt)$ferrocenyl	129	B (79)	ν(CO) 2055(A_1), 1947(A_1), 1934(E), 1976(A_1) (hexane); deep-purple c	33
$(OC)_5CrC(OMe)C_6Cl_5$	116.5	B (28)	ν(CO) 2070(A_1), 1973(A_1), 1955(E), 1966(B_1) (hexane); o c	33
$(OC)_5CrC(OEt)Ph$	29 ± 1	B	ν(CO) 2062(A_1), 1963(B_1), 1954(A_1), 1942(E) (pentane); nmr; uv; r o	29b
$(OC)_5CrC(OEt)CH_2Ph$	(Oil)	B	Made using RMgBr in place of RLi; also prepared, $^{13}C(O)$ labeled compounds; ν(CO) 2066(A_1), 1981(B_1), 1961(A_1), 1947(E); nmr; kinetic study; golden oil	29c
$(OC)_5CrC(OEt)Bu^n$	(Liq)	B	ν(CO) 2063(A_1), 1982(B_1), 1960(A_1), 1947(E) (pentane); nmr; uv; y	29b
$(OC)_5CrC(OEt)Me$	(Liq)	B	ν(CO) 2064(A_1), 1983(B_1), 1961(A_1), 1947(E) (pentane); nmr; uv; y	29b
$(OC)_5CrC(OEt)C_6Cl_5$	104	B (21)	ν(CO) 2070(A_1), 1972(A_1), 1955(E), 1998(B_1) (hexane); y-o c	33
$(OC)_5CrC(OEt)NEt_2$	29	B (~20)	ν(CO) 2034m, 1939w, 1897vs, 1870s (THF); p-y c	34

Table III (Continued)

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
$(OC)_5CrC(OSiMe_3)Me$	40 (dec)	B	ν(CO) 2058m, 1984s, 1948vs, 1912sh (Nujol); o c	30
cis-$Bu^n{}_3P(OC)_4CrC(OMe)Me$	54	D (46)	ν(CO) 2010m, 1922sh, 1909s, 1893vs (hexane); r c	39
cis-$Et_3P(OC)_4CrC(OMe)Me$	44–45	D (22)	ν(CO) 2010m, 1921sh, 1909s, 1892vs (hexane); r c	39
cis-$Et_2PhP(OC)_4CrC(OMe)Me$	56.5	D (64)	ν(CO) 2009m, 1923sh, 1910s, 1893vs (hexane); r c	39
cis-$Ph_3P(OC)_4CrC(OMe)Me$	107–108 (dec)[40]	B (48)[40]	ν(CO) 2014m, 1927s, 1908sh, 1897vs (hexane); r c	39, 40
cis-$(Hex)_3P(CO)_4CrC(OMe)Me$	117 (dec)	D (54)	ν(CO) 2007m, 1929m, 1895vs, 1877s (hexane); r c	39
cis-$Ph_3P(OC)_4CrC(OMe)Ph$		D	ν(CO) 2016m, 1927s, 1910sh, 1899vs (hexane); not isolated; r c	39
cis-$(Hex)_3P(OC)_4CrC(OMe)Ph$	114–115	D (52)	ν(CO) 2012m, 1905vs, 1890s, 1875s (hexane); r c	39
cis-$(OEt)_3P(OC)_4CrC(OMe)Me$		D	ν(CO) 2017m, 1918s, 1907vs, 1899sh (hexane); not isolated; r c	39
cis-$(p\text{-}MeC_6H_4)_3P(OC)_4CrC(OMe)Me$		D (>95)	Not isolated; yield for solution	41
$(OC)_5CrC(OMe)CH{=}CHCH{=}C(OMe)Me$	60	J (<0.1)	ν(CO) 2054m(A_1), 1949s(A_1), 1939vs(E); d-r c	42
$(OC)_5CrC(OMe)(CH{=}CH_2)$	−15 (±5)	B (44)	ν(CO) 2067(A_1), 1990w(B), 1970s(A_1), 1954vs(E) (hexane); uv; d purple c; decomposing slowly at $> -20°$	43
$(OC)_5CrC(OEt)Fu^d$	112–113	B (66)	ν(CO) 2065(A_1), 1995w(B), 1965s(A_1), 1950vs(E) (hexane); b pl	43
$(OC)_5CrC(OEt)Th^e$	134–136 (dec)	B (73)	ν(CO) 2063s(A_1), 1987w(B), 1961s(A_1), 1950vs(E) (hexane); purple pl	43
$(OC)_5CrC(OEt)(N\text{-}MePyr)^f$	136–138 (dec)	B (58)	ν(CO) 2059s(A_1), 1981w(B), 1951s(A_1), 1940vs(E) (hexane); o pl	43
$(OC)_5CrC(OCOMe)Fu^d$	71	B (50)	ν(CO) 2073m(A_1''), 2014w(B), 1988vs(E), 1979s(A_1'); nmr; uv: purple n; air- and light-sensitive	44a, 44b
$(OC)_5CrC(OMe)Fu^d$	80–81	C (70)	ν(CO) 2066m(A_1''), 1995w(B), 1950vs(E), 1966s(A_1') (hexane); nmr; uv; d-r pr	44a, 44b
$(OC)_5CrC(OPh)Fu^d$	117–118	C (92)	ν(CO) 2064m(A_1''), 1994w(B), 1961vs(E), 1965s(A_1') (hexane); nmr; uv; d-r pr	44a, 44b
$\{Me_4N[(OC)_5CrC(O)CH_2SiMe_3]$	94	B		44a
$(OC)_5CrC(OEt)CH_2SiMe_3$	(Liq)	B		
$(\pi\text{-}C_5H_5)(OC)(ON)CrC(OMe)Ph$	(Liq)	B		5
Chromium Compounds (Aminocarbene Ligands)				
$(OC)_5CrC(NH_2)Me$	76–77	C[45]	ν(CO) 2057, 1964, 1949, 1941 (hexane); preparations involve replacement of OMe[45] and $OSiMe_3$[30] groups; p-y c	30, 45
$(OC)_5CrC(NH_2)C_6H_4NMe_2\text{-}p$	154	C (76)	ν(CO) 2053(A_1), 1970(B_1), 1936(E), 1915(A_1) (hexane); y n	46
$(OC)_5CrC(NH_2)C_6H_4OMe\text{-}p$	152	C (81)	ν(CO) 2057(A_1), 1976(B_1), 1941(E), 1917(A_1) (hexane); y c	46
$(OC)_5CrC(NH_2)C_6H_4Me\text{-}p$	107	C (84)	ν(CO) 2057(A_1), 1977(B_1), 1943(E), 1920(A_1) (hexane); y c	46
$(OC)_5CrC(NH_2)Ph$	79	C (87)	ν(CO) 2058(A_1), 1978(B_1), 1944(E), 1921(A_1) (hexane); y n	46
$(OC)_5CrC(NH_2)C_6H_4Cl\text{-}p$	134	C (78)	ν(CO) 2059(A_1), 1978(B_1), 1946(E). 1923(A_1) (hexane); y c	46

Table III (Continued)

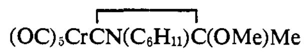
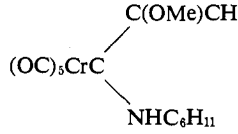
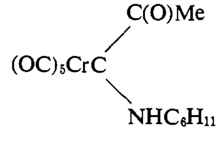
Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
$(OC)_5CrC(NH_2)C_6H_4Br$-*p*	136	C (82)	ν(CO) 2059(A_1), 1978(B_1), 1946(E), 1924(A_1) (hexane); y c	46
$(OC)_5CrC(NH_2)C_6H_4OMe$-*m*	119	C (75)	ν(CO) 2057(A_1), 1977(B_1), 1944(E), 1923(A_1) (hexane)	46
$(OC)_5CrC(NH_2)C_5H_4Cl$-*m*	111	C (84)	ν(CO) 2058(A_1), 1978(B_1), 1944(E), 1923(A_1) (hexane); y c	46
$(OC)_5CrC(NHMe)Me$		C	X-Ray, Table I; ν(CO) 2058(A_1), 1970(B), 1940(E), 1940(A_1) (hexane)	11, 16
$(OC)_5CrC(NHEt)Me$	27–29	C (59)	ν(CO) 2061(A_1), 1969(B), 1938(E), 1938(A_1) (hexane); p-y pl	16
$(OC)_5CrC(NHPr^i)Me$	88–89	C (76)	ν(CO) 2060(A_1), 1970(B), 1940(E, A_1) (hexane); prepared with $Pr^i{}_2NH$ or Pr^iNH_2; p-y pl 1918(A_1) (hexane); p-y n	16, 47
$(OC)_5CrC(NHBu^t)Me$	68–69	C (86)	ν(CO) 2058(A_1), 1965(B), 1936(E), 1918(A_1) (hexane); p-y n	16
$(OC)_5CrC(NHCH_2Ph)Me$	147–148	C (80)	ν(CO) 2058(A_1), 1968(B), 1941(E), 1938(A_1) (hexane); p-y n	16
$(OC)_5CrC(NHC_6H_4NH_2$-*p*$)Me$	144–145	C (63)	ν(CO) 2058(A_1), 1966(B), 1931(E), 1921(A_1) (hexane); y p	16
$(OC)_5CrC(NHC_6H_4OMe$-*p*$)Me$	116–117	C (73)	ν(CO) 2058(A_1), 1969(B), 1940(E), 1924(A_1) (hexane); y pr	16
$(OC)_5CrC(NHC_6H_4Me$-*p*$)Me$	120–121	C (67)	ν(CO) 2058(A_1), 1969(B), 1938(E, A_1) (hexane); y n	16
$(OC)_5CrC(NHC_6H_4Cl$-*p*$)Me$	117–118	C (52)	ν(CO) 2060(A_1), 1969(B), 1947, 1938(E), 1900(A_1) (hexane); d-y pl	16
$(OC)_5CrC(NHC_6H_3CF_3$-*p*$)Me$	127–128	C (38)	ν(CO) 2058(A_1), 1970(B), 1949, 1938(E), 1894(A_1) (hexane); d-y n	16
$(OC)_5CrC(NHC_6H_{11})Me$		C	ν(CO) 2057(A_1), 1968(B), 1936(E), 1936(A_1) (hexane)	16
$(OC)_5CrC(NHCH_2Ph)Ph$	(Oil)	C (98)	ν(CO) 2059s(A_1), 1976w(B_1), 1937vs(E), 1923vs(A_1); prepared with $PhCH_2NH_2$ or $PhCH_2NMeH$; y-g	48, 47
$(OC)_5CrC(NHBu^n)Ph$	(Oil)	C (98)	ν(CO) 2057(A_1), 1976w(B_1), 1935vs(E), 1917s(A_1); y-g	48
$(OC)_5CrC(NHPh)Ph$	85 54–5	C (70) C (10)	Two forms, cis/trans isomers, similar ir; ν(CO) 2053s(A_1), 1978w(B_1), 1934vs(E), 1919vs(A_1); o c	48
$(OC)_5CrC(NHC_6H_{11})Ph$	63	C (99)	ν(CO) 2053s(A_1), 1972w(B_1), 1928vs(E), 1915vs(A_1); lemon-y n	48
$(OC)_5CrC(NMe_2)Me$	74	C (58)	ν(CO) 2057(A_1), 1967(B_1), 1930(E, A_1) (hexane); nmr; p-y n	16, 47
$(OC)_5CrC(NEt_2)Me$	82	C (113)	ν(CO) 2056(A_1), 1966(B_1), 1929(E, A_1) (hexane); nmr; p-y pr	16, 47
$(OC)_5CrC(NMe_2)Ph$	81	C (62)	ν(CO) 2056m(A_1), 1976(B_1), 1939vs(E), 1936s(A_1) (hexane); nmr; p-y n	43a
 $(OC)_5Cr\overline{CN(C_6H_{11})C}(OMe)Me$	65.5–66.5	C (~100)	Air-sensitive y c	29a, 49
 $(OC)_5CrC(C(OMe)CH_2)(NHC_6H_{11})$	99.5–100	C (~100)	X-Ray (Table I); from above complex and benzoyl peroxide; vinyl ether group supported by AB-type ^1H nmr; y c	49, 29a
 $(OC)_5CrC(C(O)Me)(NHC_6H_{11})$	114 (dec)	C (~100)	From above complex and 2 *M* HCl–THF; ν(CO)CH_3, 1664; y c	29a, 49

Table III (Continued)

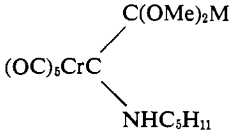
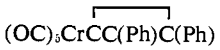
Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
	109.5–110	C	From the aziridine complex (above) and methanol; y c	49
$(OC)_5CrC(N{=}CHPh)Me$	93	C (8)	ν(CO) 2055(A_1), 1934(E, A_1) (hexane); prepared with phenylhydroxylamine; d-y n	51
$(OC)_5CrC(N{=}CMePh)Me$	103	C (16)	ν(CO) 2054(A_1), 1930(E, A_1) (hexane); prepared with methylphenylhydroxylamine; br-y n	51
$(OC)_5CrC(N{=}CPh_2)Me$	106	C (21)	ν(CO) 2054(A_1), 1930(E, A_1) (hexane); prepared with diphenylhydroxylamine; o c	51
$(OC)_5CrC(OMe)MeC_6H_{11}NC$		J	Unstable addition product of cyclohexyl isocyanide; y	29a
$(OC)_5CrC(NH_2)Fu^d$	70–71	B (54)	ν(CO) 2061s(A_1), 1978w(B), 1947s(A_1), 1942vs(E) (hexane); o n	43
$(OC)_5CrC(NH_2)Th^e$	94–94.5	B (60)	ν(CO) 2062s(A_1), 1981w(B), 1949s(A_1), 1941vs(E) (hexane); o pl	43
$(OC)_5CrC(NH_2)$-N-$MePyr^f$	128–129	B (50)	ν(CO) 2060s(A_1), 1979w(B), 1924s(A_1), 1947vs(E) (hexane); y pr	43
$(OC)_5CrC(NC_4H_8)Fu^d$	106–108	C (54)	ν(CO) 2067m(A_1'') 1978w(B), 1942vs(E), 1933s($A_1{}^1$) (hexane); Nmr; uv, y n	44b
$(OC)_5CrC(N_3)Fu^d$		B	Very sensitive to heat and light, decomposing to pentacarbonyl-(2-furanonitrile)chromium(0), mp 108°; r in solution	44a
$(OC)_5CrC(NHNMe_2)Me$		C	Proposed intermediate in reaction of $(OC)_5CrC(OMe)Me$ with NH_2NMe_2; l-y	52, 53
$(OC)_5Cr(N,N\text{-}Me_2Im)^g$	100.5	E (80)	ν(CO) 2057, 1927 (cyclohexane); stable compound; mass spectrum P^+; uv; ir; nmr; also prepared complexes of related N-heterocycles.	54
$(OC)_5CrC(OMe)N{=}CHMe$	58	C (5.7)	ν(CO) 2055m(A_1), 1936(E), 1931sh(A_1); nmr; y n	55
$(OC)_4Cr(N,N\text{-}Me_2Im)_2{}^g$	227–230	H (8)	ν(CO) 1986, 1870, 1847, 1825sh (chloroform); μ = 9.66 D	56
Chromium Compounds (Thiocarbene Ligand)				
$(OC)_5CrC(SPh)Me$	67–68	C	Similar to $(OC)_5CrC(NH_2)Me$ in physical properties; monomeric in benzene; d-brown	45
$(OC)_5CrC(SEt)Fu^d$	97–98	C (75)	ν(CO) 2057m(A_1''), 1990w(B), 1954s(E, A_1) (hexane); nmr, uv; d-violet pr	44a
$(OC)_5CrC(SPh)Fu^d$	119–120	C (79)	ν(CO) 2059m(A_1''), 1996w(B), 1962s(E), (A_1) (hexane); nmr; uv; purple n	44b
Chromium Carbene Complex not Stabilized by Heteroatom X or Y				
 $(OC)_5Cr\overline{CC(Ph)C}(Ph)$	199–200 (dec)	E (19.5)	ν(CO) 2061m, 1938vs (cyclohexane); stable; nmr; d-y c	57
Molybdenum Compounds (Oxycarbene Ligands)				
$(OC)_5MoC(OMe)Me$		B	Rapidly decomposes, y c	27
$(OC)_5MoC(OMe)Ph$		B	Chromatographically pure, rapidly decomposes; o-r c	27

Table III (Continued)

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
cis-$Ph_3P(OC)_4MoC(OMe)Me$	104–106	B	Stable by contrast with pentacarbonyl derivative; ν(CO) 2024s, 1934s, 1912s, sh, 1905vs (hexane); y-o c	40
$(\pi\text{-}C_5H_5)(OC)(ON)MoC(OMe)Ph$		B	Reaction involving transfer of carbene to iron only reported	5, 58
trans-$[(Ph_3P)(OC)_2(\pi\text{-}C_5H_5)MoFu^s]^+ Br^{-\,i}$	150–160 (dec)	J (78)	ν(CO) 1985s, 1910vs (CH_2Cl_2); J(P–H) ∼ 1.1 Hz; p-lemon-y	59
cis-$[(Ph_3P)(OC)_2(\pi\text{-}C_5H_5)Mo\text{-}Fu^s]^+ Br^{-\,i}$	140–143 (dec)	J (71)	ν(CO) 1980vs, 1910s (CH_2Cl_2); no J(P–H); br-y	59
$[(\pi\text{-}C_5H_5)(OC)_2(Hex_3P)Mo\text{-}C(OEt)Me]^+BF_4^- \cdot {}^1/_2CH_2Cl_2$		B (80)	ν(CO) 1990, 1900; y-g c	60
Compound **15**		J	X-Ray, Table I; from $Na[(\pi\text{-}C_5H_5)(CO)_3Mo]$ and diazoacetic ester; y c	24, 61
Tungsten Compounds (Oxycarbene Ligands)				
$(OC)_5WC(OMe)Me$	52	B (77)	ν(CO) 2083s, 1988s, 1946vs (Nujol); y c	27
$(OC)_5WC(OMe)Ph$	59	B (31)	ν(CO) 2079s, 1992s, 1953vs (Nujol); o c	27
cis-$Ph_3P(OC)_4WC(OMe)Me$	111.5–113	B (81)	ν(CO) 2024vs, 1925s, 1914s, 1897vs (hexane); o-r c	40
cis-$Ph_3As(OC)_4WC(OMe)Me$	116–118	B	ν(CO) 2022s, 1927s, 1912s, sh, 1901vs (hexane); y c	40
cis-$Ph_3Sb(OC)_4WC(OMe)Me$	125–129	B	ν(CO) 2024s, 1937vs, 1926s, sh, 1901vs (hexane); o-r c	40
$(\pi\text{-}C_5H_5)(OC)(ON)WC(OMe)Ph$		B		5
$(OC)_5WC(OEt)Me$	(Liq)	B		29b
$(OC)_5WC(OEt)CH_2Ph$	(Oil)	B	Made using RMgBr in place of RLi; also prepared $^{13}C(O)$ labeled compounds; ν(CO) 2075(A_1), 1984(B_1), 1957(A_1), 1945(E); nmr; kinetic study; golden oil	29c
$Ph_3P(OC)_4WC(OEt)CH_2Ph$	137–139	B	Made using RMgBr in place of RLi; nmr; golden orange	29c
$(OC)_5WC(OEt)Bu^n$	(Liq) bp 65° (0.05 mm)	B	ν(CO) 2073(A_1), 1981(B_1), 1957(A_1), 1945(E) (pentane); nmr; uv; y	29b
$(OC)_5WC(OEt)Me$	(Liq)	P	ν(CO) 2072(A_1), 1958(A_1), 1948(E), 1941(E) (pentane); nmr; uv; y	29b
Tungsten Compounds (Aminocarbene Ligands)				
trans-$(OC)_5WC(NHMe)Me$	89	C (∼65)	ν(CO) 2070s, 1980sh, 1930vs (Nujol); nmr	63
cis-$(OC)_5WC(NHMe)Me$	81	C (∼50)	ν(CO) 2066s, 1976w, sh, 1949w, sh, 1904vs (Nujol); nmr; l-y c (photosensitive)	63
trans-$Ph_3P(OC)_4WC(NHMe)Me$		C	ν(CO) 2012s, 1883vs, 1855vs (Nujol)	63
cis-$Ph_3P(OC)_4WC(NHMe)Me$	160–165	C (∼60)	ν(CO) 2004vs, 1930w, 1894vs, 1850vs (Nujol); l-y	63
Manganese Compounds (Mononuclear)				
$(\pi\text{-}C_5H_5)(OC)_5MnC(OMe)Me$	Oil, bp 60° (high vacuum)	B (18)	ν(CO) 1965vs, 1894vs (Nujol); r-b	27
$(\pi\text{-}C_5H_5)(OC)_2MnC(OMe)Ph$	Oil, bp 80–100° (high vacuum)	B (49)	ν(CO) 1969vs, 1898vs (Nujol); r-b	27
$[PhCSMn(CO)_4]_n$		J	n = 3 or 4; compound *may* have a carbene structure	64
Manganese Compounds (Binuclear)				
$(OC)_9Mn_2C(OMe)Me$	81–83	B (23)	o-r n	32, 65
$(OC)_9Mn_2C(OMe)Ph$	68	B (18)	o-y n	32
$(OC)_9Mn_2C(OEt)Me$	45	B (43)	y n	32
$(OC)_9Mn_2C(OEt)Ph$	−28	B (23)		32

Table III (Continued)

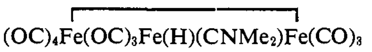
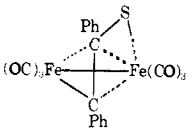
Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
$(OC)_9Mn_2C(NH_2)Me$	130	C (86)	Long-y n	32
$(OC)_9Mn_2Fu^d$	64–65	J (~28)	Originally mistaken for hydride;[67] nmr;[65] D-exchange reactions;[66] y c	65, 66, 67
Rhenium Compounds				
$(\pi-C_5H_5)(OC)_2ReC(OH)Me$	84 (dec)	B (20)	y c	68
$(\pi-C_5H_5)(OC)_2ReC(OMe)Me$	101	B (83)	$\nu(CO)$ 1972vs, 1894vs (Nujol); y c	68
$(\pi-C_5H_5)(OC)_2ReC(OMe)Bu^n$	30–32	B (25)	$\nu(CO)$ 1960vs, 1862vs (Nujol); y c	68
$(\pi-C_5H_5)(OC)_2ReC(OMe)Ph$	106	B (20)	$\nu(CO)$ 1976vs, 1892vs (Nujol); y c	68
Iron Compounds (Mononuclear)				
$(OC)_4FeC(OMe)Ph$	(Oil)	H (20)	Could not be prepared by standard methods; r-b	58
$(OC)_4FeC(OLi)Me$	−82 (dec)	B (51)	$\nu(CO)$ 2036m, 1968m, 1930s, 1862s; keto 1519s (KBr); Mp and yield refer to NMe_4^+ salt; gold-y	69
$(OC)_4FeC(OLi)Ph$	−98	B (59)	$\nu(CO)$ 2036m, 1960m, 1879s, keto 1490s; mp and yield refer to NMe_4^+ salt; o y	69, 74
$[(\pi-C_5H_5)(p-MeOC_6H_4NC)_2FeC(NHMe)NHC_6H_4OMe-p]^+$		B	PF_6^- and BF_4^- salts prepared; only 2 of 4 possible isomers observed spectroscopically; y	70
$[(\pi-C_5H_5)(p-MeOC_6H_4NC)_2FeC(NHEt)NHC_6H_4OMe-p]^+$		B	Salts not isolated; Evidence (spectroscopic) for existence in solution; y	70
$[(\pi-C_5H_5)(OC)_2FeCH_2]^+$		B	Postulated as an intermediate	71, 72
$(OC)_4Fe(N,N-Me_2Im)^g$		E		54
$[(\pi-C_5H_5)(OC)_2FeC(OH)Me]^+Cl$		B	Cream solids by protonation of acyl compounds; ir; unstable	35
$[(\pi-C_5H_5)Ph_3P(OC)FeC(OH)Me]^+X^-$		B	Cream solids (X = Cl, Br) by protonation of acyl compounds; nmr	35
$[(\pi-C_5H_5)(OC)(Hex_3P)FeC(OMe)Me]^+BF_4^-$	170 (dec)	B (~60)	$\nu(CO)$ 1995; y solid	60
$[(\pi-C_5H_5)(OC)(Ph_3P)FeC(OEt)Me]^+BF_4^-$	111 (dec)	B (~80)	$\nu(CO)$ 1990; y solid	60
$[(\pi-C_5H_5)(CO)(Hex_3P)FeC(OH)Me]^+BF_4^-$	120 (dec)	B (~80)	$\nu(CO)$ 1961; y c	60
$[(\pi-C_5H_5)(OC)(Hex_3P)FeC(OEt)Me]^+BF_4^-$	175 (dec)	B (~90)	(CO) 1965; y solid	60
$(Ph_3P)(OC)_3FeC(OEt)Me$		B	$\nu(CO)$ 1905, 1897	73
$(Ph_3P)(OC)_3FeC(OEt)Ph$		B	$\nu(CO)$ 1913, 1898	73
Iron Compounds (Binuclear) (see footnotes)				
$(OC)_9Fe_2C(Ph)H$	111	B (0.5)	Ir depends on conformation; mass spectrum P^+; o-r	69, 74
$(OC)_6Fe_2(COCH_3)_2$	Dec room temp	B	$\nu(CO)$ 2083m, 2038s, 2006s, 1970s, keto 1536 (hexane)	69
$(OC)_6Fe_2(COPh)_2$		B	X-Ray, Table II; $\nu(CO)$ 2083m, (hexane); r-b	69
 $(OC)_4Fe(OC)_3Fe(H)(CNMe_2)Fe(CO)_3$	162–164 (dec)	I	$\nu(CO)$ 2080–1978	62
$(Et_2NH)(OC)_5Fe_2(COPh)_2$				75
$(Et_2NH)(CO)_5Fe_2(NEt_2CO)_2$	105	B (59)	$\nu(CO)$ 2070m, 2026s, 1994s, 1956m (hexane); r-b	76
	125–126 (dec)	J	X-Ray, Table II; $\nu(CO)$ 2066, 2033, 2010, 1957 (KBr); o c	19
$(\pi-C_5H_5)(OC)Fe(CHNMe)_2BH_2$	123–124	B (50)	$\nu(CO)$ 1950; y	70a
Ruthenium Compounds				
$[(\pi-C_5H_5)(CO)(Hex_3P)RuC(OH)Me]^+BF_4^- \cdot H_2O$		B (~70)	$\nu(CO)$ 1965; w	60
$[(\pi-C_5H_5)(OC)(Hex_3P)RuC(OEt)Me]^+BF_4^-$	200 (dec)	B (75)	$\nu(CO)$ 1968; w	60
$Ru_3(OC)_9H(C_6H_5CC_6H_4)$	139–142	B (1)	X-Ray, Table II; r c	20
Cobalt Compounds				
$Ph_3Sn(OC)_3CoC(OEt)Ph$	122–124	1	$\nu(CO)$ 1967, 1955; air-stable; M 620; y c	73
Porphyrin **5** 21, 23 cis, trans to carbene	213–215	5 (3)	Air-stable purple-blue crystals; $\nu(C{=}O)$ 1700, 1705sh, λ_{max} 407, 420sh, 512, 554 nm; ϵ_{max} 35,400, 32,600, 6000, 6400; mass spectrum P^+; nmr	77

Table III (Continued)

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
Porphyrin **6** 21, 22 cis and trans	203–205	5 (14)	Air-stable purple-blue crystals; ν(C=O) 1715, 1703sh; λ_{max} 406, 578, 554 nm; nmr	77
		Rhodium Compounds		
$(Ph_3P)_2ClRh(N,N\text{-}Ph_2Im^{\bullet})^k$	209 (dec)	F (80)	ν(RhCl) 287; yield from 4 crystallizations; o c; bromo-analog also made	78
$(Ph_3P)(OC)ClRh(N,N\text{-}Ph_2Im^{\bullet})^k$	198	F (70)	ν(CO) 1973; ν(RhCl) 299 (Nujol); nmr; y c	78
$(Ph_3P)_2ClRh[N,N\text{-}(C_6H_4Me\text{-}p)_2Im^{\bullet}]^k$	195–200	F (80)	ν(RhCl) 300 (Nujol)	78
$[(OC)Cl_3RhC(Ph)N(Me)C(Ph){=}NMe]_2$	>300	G (73)	Also + $2CH_2Cl_2$; X-ray; MW; ν(CO) 2120; ν(CN) 1656, 1502; ν(RhCl) 355vs, 332m, 315w (Nujol); nmr; p-y c	79
$[(OC)Cl_3Rh\text{-}C(Ph)N(Et)C(Ph){=}NMe]_2$	>300	G (69)	ν(CO) 2120; ν(CN) 1648, 1497; ν(RhCl) 349s, 316m (Nujol); nmr; y c	79
$[(OC)Br_3Rh\text{-}C(Ph)N(Me)C(Ph){=}NMe]_2$	>300	D (82)	ν(CO) 2115; ν(CN) 1648, 1492 (Nujol); nmr; o c	79
$[(OC)I_3Rh\text{-}C(Ph)N(Me)C(Ph){=}NMe]_2$	240–224	D (57)	ν(CO) 2080; ν(CN) 1638, 1470 (Nujol); nmr; d-r cubes	79
$(Me_2PhP)_2Cl_3Rh\text{-}C(Ph)N(Me)C(Ph){=}NMe$	187–189	D (34)	ν(CN) 1651, 1470; ν(RhCl) 323w, 298m (Nujol); nmr; y c	79
$[(OC)Cl_3RhC(Ph)NHMe]_n$	>190 (dec)	G (69)	ν(NH) 3165; ν(CO) 2120; ν(CN) 1612; ν(RhCl) 355m, 340w, 324w, 297w (Nujol); nmr; y c	79
$[(OC)Cl_3RhC(Ph)NHPr^i]_n$	160 (dec)	C (59)	ν(NH) 3110; ν(CO) 2120; ν(CN) 1602; ν(RhCl) 360s, 320m, 301w, 255m (Nujol); y c	79
$[(OC)Cl_3RhC(Me)NHC_6H_4Me\text{-}o]_n$	>200 (dec)	G (49)	ν(NH) 3115; ν(CO) 2125; ν(CN) 1570; ν(RhCl) 369m, 355w, 325m, 304m, 288m, 252m (Nujol); o-y	79
$(Me_2PhP)_2Cl_3RhC(Me)NHC_6H_4Me\text{-}o$	289–291	D (29)	ν(NH), 3110; ν(CN) 1529; ν(RhCl) 330m, 301w, 273m (Nujol); nmr; y c	79
$(Ph_3P)(OC)Cl_3RhC(Ph)NHMe$	168–171	G (85)	ν(NH) 3120; ν(CO) 2105; ν(CN) 1598; ν(RhCl) 324m, 293s (Nujol); nmr; w c	79
$(Ph_3P)(OC)Cl_3RhC(Ph)NHEt$	164–167	G (65)	ν(NH) 3130; ν(CO) 2105; ν(CN) 1599; ν(RhCl) 330w, 299m, 283w (Nujol); nmr; w c	79
$(Ph_3P)(OC)Cl_3RhC(Ph)NHPr^i$	162–164	G (79)	ν(NH) 3100; ν(CO) 2100; ν(CN) 1596; ν(RhCl) 324m, 286s (Nujol); nmr; w c	79
$(Ph_3P)(OC)Cl_3RhC(Me)NHC_6H_4Me\text{-}o$	>200	G (47)	76% yield for complex + CH_2Cl_2; ν(NH) 3140 (3095 of CH_2Cl_2 adduct); ν(CO) 2105; ν(CN) 1560 (1571 of CH_2Cl_2 adduct); ν(RhCl) (CH_2Cl_2) 306m, 297m, 273m (Nujol); nmr; p-y c	79
$(MePh_2P)(OC)Cl_3RhC(Ph)NHMe$	160–163	G (42)	ν(NH) 3135; ν(CO) 2100; ν(CN) 1607; ν(RhCl) 324m, 285s (Nujol); nmr; colorless crystals	79
		Iridium Compounds		
$(Ph_2Me)_2(OC)ClIrC(CF_3)_2$	154	F (37)	J(P-F) = 10 Hz; ν(CO) 2056; cream colored	80
$(Ph_3P)_2(OC)ClIrCH_2$		F	Proposed as intermediate	81
		Nickel Compound		
$[(OC)NiC(OMe)Ph]_3$		H	Violet, diamagnetic, very air-sensitive product	58

Table III (Continued)

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
		Palladium Compounds		
cis-(PhNC)Cl$_2$PdC(PhNH)OMe	165	B (65)	ν(C≡N) 1554s; off-w	82
cis-(Ph$_3$P)Cl$_2$PdC(PhNH)OMe	159	B (80)	ν(C≡N) 1547s; off-w	82
cis-(PhNC)Cl$_2$PdC(PhNH)HNC$_6$H$_4$Me-*p*	234	B (80)	ν(C≡N) 1548s; off-w	82
cis-(Ph$_3$P)Cl$_2$PdC(PhNH)NHC$_6$H$_4$Me-*p*	249	B (70)	ν(C≡N) 1538; w	
cis-(MeNC)$_2$Pd[MeNHCNHNC=NHMe]$^+$Cl · $^2/_3$H$_2$O		B (61)	d-o	83
cis-Cl$_2$Pd[MeNHCNHNHCNHMe]		B	The analogous perchlorate and iodide were also prepared; X-ray, Table II	3
			No ir absorptions 3000–1652; no ν(C≡N); also prepared were complexes of the 4-Me and 4-Ph derivatives of the 3,6-σ-2,4,5,7-tetraazaocten-3,3,6-triyl ligand; y	83
trans-Cl$_2$-μ-Cl$_2$Pd$_2$($\overline{\mathrm{CC(Ph)C}}$(Ph))$_2$	215 (dec)	G (76)	l-y c	84
trans-(C$_6$H$_{11}$)$_3$PCl$_2$Pd$\overline{\mathrm{CC(Ph)C}}$(Ph)		D	Also analogs with MeCN, C$_2$H$_4$O, pyridine, and Me$_2$SO in place of the phosphine; not isolated	84
trans-(PhNC)(Cl$_3$Sn)$_2$PdC(NHPh)-NHC$_6$H$_4$Me-*p*	212 (dec)	D	y c	85
trans-(Ph$_3$P)(Cl$_3$Sn)$_2$PdC(NHPh)-NHC$_6$H$_4$Me-*p*	203 (dec)	D	y c	85
cis-(Ph$_3$P)Cl$_2$PdC(NHC$_6$H$_4$NO$_2$-*p*)-NHC$_6$H$_4$Me-*p*	237 (dec)	B	p-y c	85
trans-(Et$_3$P)Cl$_2$Pd(*N*,*N*-Ph$_2$Im^s)[k]	197–200	F (17)	ν(Pd–Cl) 351s, 318w; ν(Pd–P) 415w (Nujol); nmr; y c	86
cis-(Et$_3$P)Cl$_2$Pd(*N*,*N*-Ph$_2$Im^s)[k]	275–290	I (81)	ν(Pd–Cl) 302s, 272s; ν(Pd–P) (Nujol) 435; w n	86
trans-(Et$_3$P)Br$_2$Pd(*N*,*N*-Ph$_2$Im^s)[k]	190–191	F (65)	ν(Pd–P) 418w (Nujol); nmr; y c	86
cis-(Et$_3$P)Cl$_2$Pd(*N*,*N*-Me$_2$Im^s)[k]	245 (dec)	I (24)	ν(Pd–Cl) 309s, 285s, 279sh; ν(C=N) 1528vs (Nujol); nmr; w c	86
cis-(Et$_3$P)Cl$_2$Pd(*N*-MeBzT)[h]	200–255 (dec)	I (57)	ν(Pd–Cl) 311s, 280s (Nujol); w c	86
		Platinum Compounds		
cis-(Et$_3$P)Cl$_2$Pt[C(OMe)NHPh]	194–195	B (60)	ν(Pt–Cl) 305, 275 (Nujol); w	14
cis-(Et$_3$P)Cl$_2$Pt[C(OEt)NHPh]	209–211	B (90)	X-Ray, Table II; ν(Pt–Cl) 306, 284 (Nujol); w	14
cis-(Et$_3$P)Cl$_2$Pt[C(OPr^i)NHPh]	108–110	B (40)	ν(Pt-Cl) 305–283 (Nujol); w	14
cis-(Et$_3$P)Br$_2$Pt[C(OEt)NHPh]	115–117	B (80)	ν(Pt–Br) 201, 192; w n	14
cis-(Pr$^n{}_3$P)Cl$_2$Pt[C(OEt)NHPh]	196–198	B (50)	w	14
cis-(Et$_3$P)Cl$_2$Pt[C(NHPh)$_2$]	235–236	B (40)	ν(Pt–Cl) 305, 278 (Nujol); w	14
cis-(Et$_3$P)Cl$_2$Pt[C(NHBu^s)NHPh]	253–255	B (60)	ν(Pt–Cl) 306, 284 (Nujol); w	14
cis-(Et$_3$P)Cl$_2$Pt[C(NHEt)NHPh]	248–250	B (50)	ν(Pt–Cl) 295, 275 (Nujol); w	14
cis-(Pr$_3$P)Cl$_2$Pt[C(NHPh)$_2$]	137–139	B (40)	w	14
cis-(Et$_3$P)Cl$_2$Pt[C(NHMe)NHPh]	142–144	B (70)	ν(Pt–Cl) 294–270 (Nujol); w	14
cis-(Et$_3$P)Cl$_2$Pt[C(NHMe)NHEt]	137–140	B (60)	w	14
cis-(Et$_3$P)Cl$_2$Pt[C(OMe)NHPh]	189–192	B (80)	w	14
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)Me]PF$_6$	148–150	B	ν(C–O) 1315; ν(Pt–C) 514; nmr; w c	87, 88
trans-[Me(Me$_3$As)$_2$PtC(OMe)Me]PF$_6$	170–172	B	ν(C–O) 1305; ν(Pt–C) 514; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OEt)Me]PF$_6$	152–154	B	ν(C–O) 1310; ν(Pt–C) 519; nmr; w c	87, 88
trans-[Me(Me$_3$As)$_2$PtC(OEt)Me]PF$_6$	170–172	B	ν(C–O) 1315; ν(Pt–C) 523; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)Et]PF$_6$	155	B	ν(C–O) 1300; ν(Pt–C) 521; nmr; w c	87, 88
trans-[Me(Me$_3$As)$_2$PtC(OMe)Et]PF$_6$	140	B	ν(C–O) 1310; ν(Pt–C) 516; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)Pr^n]PF$_6$	148–149	B	ν(C–O) 1300; ν(Pt–C) 516; nmr; w c	87, 89

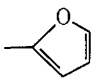
Table III (Continued)

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
trans-[Me(Me$_3$As)$_2$PtC(OMe)Pr^n]PF$_6$	150	B	ν(C–O) 1310; ν(Pt–C) 519; nmr; w c	87, 89
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)Bu^n]PF$_6$	136	B	ν(C–O) 1305; ν(Pt–C) 523; nmr; w c	87, 89
trans-[Me(Me$_3$As)$_2$PtC(OMe)Bu^n]PF$_6$	125–126	B	ν(C–O) 1310; ν(Pt–C) 516; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)*n*-C$_5$H$_{11}$]PF$_6$	120–122	B	ν(C–O) 1290; ν(Pt–C) 514; nmr; w c	87, 88
trans-[Me(Me$_3$As)$_2$PtC(OMe)-*n*-C$_5$H$_{11}$]PF$_6$	100	B	ν(C–O) 1310; ν(Pt–C) 514; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)CH$_2$C$_6$H$_{11}$]PF$_6$	114	B	ν(C–O) 1300; ν(Pt–C) 514; nmr; w c	87, 88
trans-[Me(Me$_3$As)$_2$PtC(OMe)CH$_2$C$_6$H$_{11}$]PF$_6$	152	B	ν(C–O) 1320; ν(Pt–C) 516; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OMe)CH$_2$Ph]PF$_6$	150	B	ν(C–O) 1290; ν(Pt–C) 526; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$PtC(OEt)CH$_2$Ph]PF$_6$	185–190	B	ν(C–O) 1290; ν(Pt–C) 516; nmr; w c	87, 88
trans-[Me(Me$_2$PhP)$_2$Pt$\overline{\mathrm{C(OCH_2CH_2C}}\mathrm{H_2)}$]PF$_6$	155	J	Crystalline solid; w ν(C–O) 1260; ν(Pt–C) 523; nmr; w c	88
trans-[Me(Me$_3$As)$_2$Pt$\overline{\mathrm{C(OCH_2CH_2C}}\mathrm{H_2)}$]PF$_6$	153–155	J	Crystalline solid; w ν(C–O) 1255; ν(Pt–C) 514	88
trans-[(EtNC)(Me$_2$PhP)$_2$PtC(OEt)NHEt]-(PF$_6$)$_2$		B (∼40)	ν(NH) 3382; ν(N≡C) 2271; nmr; w c	88a
trans-[(EtNC)(Me$_2$PhP)$_2$PtC(NHPh)NHEt]-(PF$_6$)$_2$		B (∼40)	ν(NH) 3341, 3389; ν(N≡C) 2265; nmr; w c	88a
trans-[(EtNC)(Me$_2$PhP)$_2$PtC(NHC$_6$H$_4$Me-*p*)-NHEt](PF$_6$)$_2$		B (∼40)	ν(NH) 3346, 3393; ν(N≡C) 2264; nmr; w c	88a
trans-[(EtNC)(Me$_2$PhP)$_2$PtC(SCH$_2$Ph)-(NHEt)](PF$_6$)$_2$		B (∼40)	ν(NH) 3342; ν(N≡C) 2257; nmr; w c	88a
cis-(MeNC)$_2$Pt[MeNHCNHN=CNHMe]$^+$-Cl$^-\cdot$4H$_2$O		B (78)	Also prepared were the anhydrous compound, and the BPh$_4^-$ salt; o-r n	83
cis-(MeNC)$_2$Pt[MeNHCNMeN=CNHMe]$^+$Cl$^-$		B (93)	o	83
cis-(MeNC)$_2$Pt[MeNHCNPhN=CNHMe]$^+$Cl		B (67)	o	83
cis-(α,α'-bipyl)Pt[MeNHCNHN=CNHMe]$^+$Cl		D (93)	o-b pr	83
cis-(MeNC)$_2$Pt[MeNHCN(CONH$_2$)-NCNHMe]$^+$Cl		B	Also prepared were the azide and perchlorate; rc	83
cis-(Ph$_2$PCH$_2$)$_2$Pt[MeNHCNHN=CNHMe]$^+$Cl		D (91)	Yellow needles; also prepared were the nitrate and tetraphenylborate analogs; y c	83
cis-{(MeNC)$_2$Pt[MeNHCNHN=CNHMe]}$^+$-AsPh$_4$		D (90)	y n	83
cis-Cl$_2$Pt[MeNHCNHNHCNHMe]		D (83)	Also prepared were picrate and methylammonium picrate derivatives; p y	83
cis-Cl$_2$Pt[MeNHCNMeNHCNHMe]		B	w	83
cis-Cl$_2$Pt[MeNHCNPhNHCNHMe]		B	w	83
cis-I$_2$Pt[MeNHCNHNHCNHMe]		C (92)	w n	83
cis-X{Pt[MeNHCNHN=CNHMe]}		D (75)[i]	X = dimethyl glyoxímate, also prepared were X = 8-quinolinato and salicylaldoximato; leaflets	83
cis-(*p*-MeC$_6$H$_4$NC)Cl$_2$PtC(OMe)-NHC$_6$H$_4$Me-*p*	158	B	ν(Pt–Cl) 328m, 294m; y c	89
cis-(C$_6$H$_{11}$NC)Cl$_2$PtC(OMe)NHC$_6$H$_{11}$	105–115 (dec)	B	ν(Pt–Cl) 325m, 291m; w c	89
cis-(C$_6$H$_{11}$NC)Cl$_2$PtC(NHC$_6$H$_{11}$)-NHC$_6$H$_4$Me-*p*	124	B	ν(Pt-Cl) 320s; off-w	85
trans-(C$_6$H$_{11}$NC)(Cl$_3$Sn)$_2$PtC(NHC$_6$H$_{11}$)-NHC$_6$H$_4$Me-*p*	∼152	D	ν(M–Cl) 335s, 322m; o	85
cis-(Et$_3$P)Cl$_2$Pt(*N*,*N*-Me$_2$Im[s])[k]	∼280 (dec)	F (21)	ν(Pt–Cl) 312vs, 288vs; ν(Pt–P) 435m; ν(C=N) 1527vs, 1505sh (Nujol); *J*(Pt–P) = 3.72 kHz; w c	86

Table III (Continued)

Compound	*Mp, °C*	*Method of prepn*[b] *(yield, %)*	*Selected data*[c]	*Ref*
trans-$(\mathrm{Et_2P})\mathrm{Cl_2Pt}$(*N*-MeBzT)[h]	156–158	F (25)	ν(Pt–Cl) 347s, 320s; ν(Pt–P) 435s, 430sh (Nujol); *J*(Pt–P) = 2.44 kHz; y c	86
cis-$(\mathrm{Et_3P})\mathrm{Cl_2Pt}$(*N*-MeBzT)[h]	280 (dec)	I (46)	ν(Pt–Cl) 310s, 302sh, 281s; ν(Pt–P) 435m (Nujol); pink c	86
trans-$(\mathrm{Et_3P})\mathrm{Br_2Pt}$(*N*-MeBzT)[h]	171–173	F (20)	ν(Pt–P) 431s (Nujol); y c	86
cis-$(\mathrm{Et_3P})\mathrm{Br_2Pt}$(*N*-MeBzT)[h]	250–275 (dec)	I (50)	ν(Pt–P) 437m (Nujol); pink c	86
(*p*-$\mathrm{MeC_6H_4NC})\mathrm{Cl_2PtC(NHC_6H_4Me}$-*p*$)_2$	217	B	ν(Pt–Cl) 328s, 320sh; w	85
(*p*-$\mathrm{MeC_6H_4NC})\mathrm{Cl_2PtC(NHC_6H_4Me}$-*p*$)_2$	134 (dec)	B	ν(Pt–Cl) 331vs; p y	85
trans-$(\mathrm{C_6H_{11}NC})(\mathrm{Cl_3Sn})_2\mathrm{PtC(OMe)NHC_6H_{11}}$	145–147	D	ν(M–Cl) 335vs; w	85
$(\mathrm{C_6H_{11}NC})\mathrm{Cl_2PtC(OEt)NC_6H_{11}}$	131	B	w	85
trans-$(\mathrm{Et_2P})\mathrm{Cl_2Pt}$(*N*,*N*-$\mathrm{Ph_2Im^s}$)[k]	201	F (50)	X-Ray, Table II; ν(Pt–Cl) 341s, 326sh; ν(Pt–P) 422w (Nujol); *J*(Pt–P) = 2.44 kHz; y n	86
cis-$(\mathrm{Et_3P})\mathrm{Cl_2Pt}$(*N*,*N*-$\mathrm{Ph_2Im^s}$)[k]	308–310 (dec)	I (100)	X-Ray, Table III; ν(Pt–Cl) 308s, 277s; ν(Pt–P) 439m (Nujol); w c	90
trans-$(\mathrm{Et_3P})\mathrm{Br_2Pt}$(*N*,*N*-$\mathrm{Ph_2Im^s}$)[k]	187–190	F (64)	ν(Pt–P) 420m (Nujol); nmr; y c	86
cis-$(\mathrm{Et_3P})\mathrm{Br_2Pt}$(*N*,*N*-$\mathrm{Ph_2Im^s}$)[k]	310–315	I (90)	ν(Pt–P) 438m (Nujol); w c	90
trans-$(\mathrm{Et_3P})\mathrm{Cl_2Pt}$(*N*,*N*-$\mathrm{Me_2Im^s}$)[k]	183–185	F (69)	ν(Pt–Cl) 339vs, 326sh; ν(Pt–P) 421m; ν(C=N) 1531vs, 1510s (Nujol); *J*(Pt–P) = 2.35 kHz; y n	86
$[(\mathrm{Ph_3P})_2\mathrm{IPtC(Ph)NHMe}]^+\mathrm{PF_6}^-$	280–282	B (80)	w c	89a
		Mercury Compounds		
$[\mathrm{Hg}$(*N*,*N*-$\mathrm{Ph_2Im})_2]^{2+}(\mathrm{ClO_4}^-)_2$	370 (dec)	E (95)	Colorless plates; mass spectral study; also prepared was the Cl^- analog mp 290–295°	91, 92
$[\mathrm{ClHg}$(*N*,*N*-$\mathrm{Ph_2Im})]^+\ \mathrm{Cl}^-$	305–310 (dec)	E (61)		92
$\mathrm{Bu^n{}_2Hg[C(OLi)NEt_2]}$		?	Postulated as an intermediate	93
$\{\mathrm{Hg[C(OMe)NEt_2]}\}^{2+}(\mathrm{BF_4}^-)_2$	207	B	Crystals; τ(N–CH) 5.99q, 6.21q; $\tau(\mathrm{O{-}CH_2})$ 5.43s	94
$\{\mathrm{Hg[C(OEt)NEt_2]}\}^{2+}(\mathrm{BF_4}^-)_2$	202	B	Crystals; τ(N–CH), 6.02q, 6.25q; $\tau(\mathrm{O{-}CH_2})$ 5.14q; also prepared was the $\mathrm{ClO_4}^-$ analog	94
$\{\mathrm{Hg[C(OEt)N(Me)CH_2Ph]_2}\}^{2+}(\mathrm{BF_4}^-)_2$	228	B	Crystals; τ(N–CH) 5.06s, 6.37s; τ(O–CH) 5.02q	94
$\{\mathrm{Hg[C(NHMe)NR_2]_2}\}^{2+}(\mathrm{OAc}^-)_2$		B	Particular R not specified; prepared from $\mathrm{Hg(OAc)_2}$, $2\mathrm{R_2NH}$, and 2MeNC	95

[a] Where carbene complexes are prepared by route B, involving modification of a carbonyl ligand, the intermediate salts [*e.g.*, $(\mathrm{LM}_n\mathrm{{-}C(O)R})^-\mathrm{Li}^+$] are not separately described here. Details may be found in the references cited for the neutral carbene complexes. [b] The letters B–J in this column refer to the methods discussed in sections III.B–J. Binuclear complexes of iron are included here for comparison; we do not regard them as carbene complexes by virtue of the sp^3 carbon of the ligands (*e.g.*, >C(Ph)H. [c] Ir data are in cm^{-1}; ν(CO) refers to stretching mode of coordinated carbonyls; ν(C=O), $\nu(\mathrm{C\overset{\cdots}{-}O})$ specified. Symmetry classes of ν(CO) are given where literature assignments are reported. Mulling media and solvents are given when available. For the nmr data, ^{1}H chemical shifts are on τ scale; abbreviations are s, singlet: d, doublet; t, triplet; q, quartet; m, multiplet. MW = molecular weight, μ = dipole moment (Debye). Of the compounds in the table. the neutral compounds generally give parent ions in the mass spectrum except for complexes of triphenylphosphine, but exceptions to this rule are noted. Data are not available. however, for compounds reported in ref 19, 56, 59, 70, 82, and 89. The colors of the complexes are given wherever they have been reported. The following abbreviations are used: r = red, o = orange, y = yellow, g = green, w = white; br = bright, d = deep, l = light, p = pale. Crystalline forms are abbreviated: c = crystals, n = needles, pl = plates, pr = prisms. [d] Fu = 2-furoyl (i). [e] Th = 2-thienyl (ii). [f] *N*-MePyr = *N*-methylpyrolyl (iii). [g] Im = imidazolidylidene (iv). [h] BzT = benzothiazolylidene (v). [i] For X =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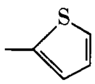
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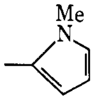
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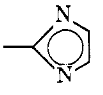
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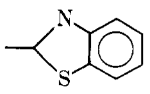
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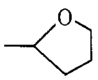
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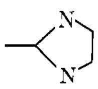
vii

dimethylglyoximate. [j] $\mathrm{Fu^s}$ = tetrahydrofuroylidene(vi). [k] $\mathrm{Im^s}$ = dihydroimidazolidylidene(vii).

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(35) M. L. H. Green and C. R. Hurley, *J. Organometal. Chem.*, **10**, 188 (1967).

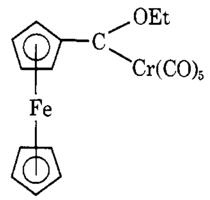
(36) E. O. Fischer, *Proc. Int. Conf. Coord. Chem., 11th*, E7, 353 (1968).

(37) C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, **7**, 390 (1968).

(38) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Müller, and R. D. Fischer, *J. Organometal. Chem.*, **28**, 237 (1971).

(39) H. Werner and H. Rascher, *Inorg. Chim. Acta*, **2**, 181 (1968).

(40) E. O. Fischer and R. Aumann, *Chem. Ber.*, **102**, 1495 (1969).



3

$$\mathrm{Cr(CO)_6 + LiNEt_2 \xrightarrow{(Et_2O)} (OC)_5CrC(OLi)NEt_2.Et_2O \xrightarrow[(CH_2Cl_2)]{Et_3OBF_4} (OC)_5CrC(OEt)NEt_2 + LiBF_4 + Et_2O} \quad (6)$$

A variation of this route involves treatment of *neutral* acyl compounds either with acids and then diazomethane or with oxonium salts, affording salts of the corresponding carbene complexes,[35] illustrated in eq 7. Related acyl compounds, *e.g.*,

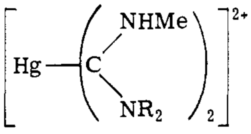
$$\pi\text{-}\mathrm{C_5H_5(OC)_2FeCOMe + HCl} \longrightarrow [\pi\text{-}\mathrm{C_5H_5(OC)_2FeC(OH)Me]^+Cl^-} \quad (7)$$

of platinum may be expected to behave similarily.

Isonitrile ligands, like carbonyls, have been modified to afford many carbenes, the reagents most often employed being alcohols or primary or secondary amines. Reactions of this type involved methyl isonitrile coordinated to platinum, as shown in eq 8.[14] The method has been extended to palladium compounds;[82,85,89] and for Hg,[85,93–95] as well as Fe[70,70a] and Pt,[2,83] the *in situ* reaction, without isolation of intermediate isonitrile complexes, also gives excellent yields, as in eq 9.[63]

$$cis\text{-}\mathrm{(PEt_3)Cl_2Pt(CNMe) + EtOH} \longrightarrow cis\text{-}\mathrm{(PEt_3)Cl_2PtC(OEt)NHMe} \quad (8)$$

$$\mathrm{Hg(OAc)_2 + 2R_2NH + 2MeNC} \longrightarrow$$



$$[\mathrm{Hg\{C(NHMe)(NR_2)\}_2]^{2+}(OAc^-)_2} \quad (9)$$

The syntheses of the Chugaev salts is another example of this type. However, isonitrile complexes of Cr(0) and Mo(0) do not react with alcohols or amines. Treatment with LiBu-*n* followed by $\mathrm{Me_3OBF_4}$ yielded a complex mixture whose composition is unknown.[93a]

A particularly interesting recent synthesis involves the conversion of a γ-bromoalkylmetal complex into an alkoxycarbene–metal cationic complex, probably *via* CO insertion and subsequent SNi rearrangement, as illustrated in eq 10.[59]

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(41) H. Werner and H. Rascher, *Helv. Chim. Acta*, **51**, 1765 (1968).

(42) L. Knauss and E. O. Fischer, *J. Organometal. Chem.*, **31**, C71 (1971).

(43) J. A. Connor and E. M. Jones, *J. Chem. Soc. A*, 1974 (1971).

(43a) J. A. Connor and J. P. Lloyd, *ibid.*, 3237 (1970).

(43b) J. A. Connor and P. D. Rose, *Tetrahedron Lett.*, 3623 (1970).

(44) (a) J. A. Connor and E. M. Jones, *Chem. Commun.*, 570 (1971); (b) *J. Chem. Soc. A*, 3368 (1971).

(45) U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, **89**, 7141 (1967).

(46) E. O. Fischer and H. J. Kollmeier, *Chem. Ber.*, **104**, 1339 (1971).

(47) J. A. Connor and E. O. Fischer, *Chem. Commun.*, 1024 (1967).

(48) E. O. Fischer, B. Heckl, and H. Werner, *J. Organometal. Chem.*, **28**, 359 (1971).

(49) R. Aumann and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **6**, 879 (1967).

(50) E. O. Fischer and V. Kiener, *ibid.*, **6**, 961 (1967).

(51) L. Knauss and E. O. Fischer, *Chem. Ber.*, **103**, 1262, 3744 (1970).

(52) E. O. Fischer and R. Aumann, *ibid.*, 101, 963 (1968).

(53) E. O. Fischer and R. Aumann, *Angew. Chem., Int. Ed. Engl.*, **6**, 181 (1967).

(54) K. Öfele, *J. Organometal. Chem.*, **12**, P42 (1968); *Angew. Chem., Int. Ed. Engl.*, **8**, 916 (1969).

(55) L. Knauss and E. O. Fischer, *J. Organometal. Chem.*, **31**, C68 (1971).

(56) K. Öfele and M. Herberhold, *Angew. Chem., Int. Ed. Engl.*, **9**, 739 (1970).

(57) K. Öfele, *ibid.*, 7, 950 (1968).

(58) E. O. Fischer and H. J. Beck, *ibid.*, **9**, 72 (1970); H. J. Beck, Dissertation, Technische Hochschule München.

(59) F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, **93**, 2672 (1971).

(60) M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, 794 (1971).

(61) M. L. H. Green and J. R. Sanders, *Chem. Commun.*, 956 (1967); *J. Chem. Soc. A*, 1947 (1971).

(62) R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Commun.*, 1193 (1970).

(63) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **16**, 275 (1969).

(64) E. Lindner, H. Weber, and H. G. Karmann, *ibid.*, **17**, 303 (1969).

(65) C. P. Casey and R. L. Anderson, *J. Amer. Chem. Soc.*, **93**, 3554 (1971).

(66) C. P. Casey, *Chem. Commun.*, 1220 (1970).

(67) R. B. King, *J. Amer. Chem. Soc.*, **85**, 1922 (1963).

(68) E. O. Fischer and A. Riedel, *Chem. Ber.*, **101**, 156 (1968).

(69) E. O. Fischer and V. Kiener, *J. Organometal. Chem.*, **23**, 215 (1970).

(70) R. J. Angelici and L. M. Charley, *ibid.*, **24**, 205 (1970).

(70a) P. M. Treichel and J. P. Stenson, *Chem. Commun.*, 423 (1969).

(71) P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 5044 (1966).

(72) M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. A*, 1508 (1967).

(73) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).

(74) E. O. Fischer, V. Kiener, and R. D. Fischer, *J. Organometal. Chem.*, **16**, P60 (1969).

(75) V. Kiener, Dissertation, Technische Hochschule München, 1969.

(76) E. O. Fischer and V. Kiener, *J. Organometal. Chem.*, **27**, C56 (1971).

(77) P. L. Batten, A. W. Johnson, and M. Mahendran, unpublished observations; A. W. Johnson, *Pure Appl. Chem., Suppl.*, **6**, 101 (1971).

(78) D. J. Cardin, M. J. Doyle, and M. F. Lappert, unpublished observations.

(79) M. F. Lappert and A. J. Oliver, *Chem. Commun.*, 274 (1972).

(80) J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *ibid.*, 170 (1968); *J. Chem. Soc. A*, 1872 (1969).

(81) F. D. Mango and I. Dvoretzky, *J. Amer. Chem. Soc.*, **88**, 1654 (1966).

(82) B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, **9**, 2021 (1970).

(83) G. Rouschias and B. L. Shaw, *J. Chem. Soc. A*, 2097 (1971).

(84) K. Öfele, *J. Organometal. Chem.*, **22**, C9 (1970).

(85) F. Bonati, G. Minghetti, T. Boschi, and B. Crociani, *ibid.*, **25**, 255 (1970).

(86) D. J. Cardin, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, in press.

(87) M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Commun.*, 809 (1971).

(88) M. H. Chisholm and H. C. Clark, *ibid.*, 763 (1970); *Inorg. Chem.*, **10**, 1711 (1971).

(88a) H. C. Clark and L. E. Manzer, *J. Organometal. Chem.*, 30, C89 (1971).

(89) F. Bonati and G. Minghetti, *ibid.*, 24, 251 (1970).

(89a) P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *Chem. Commun.*, 1627 (1970).

(90) B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, to be published.

(90a) D. J. Cardin, B. Çetinkaya, and M. F. Lappert, to be published.

(91) H. W. Wanzlick and H. J. Schönherr, *Angew. Chem., Int. Ed. Engl.*, 7, 141 (1968).

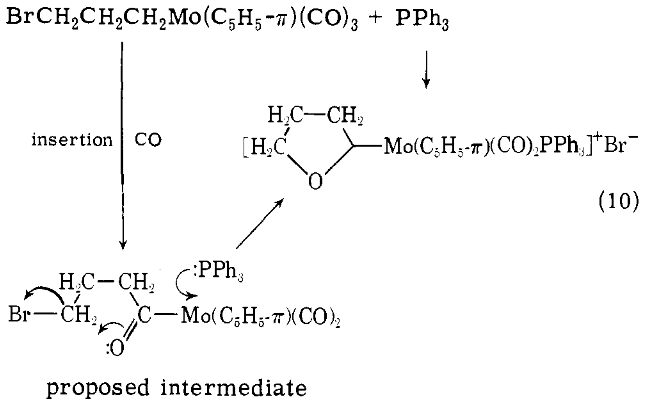
(92) H. W. Wanzlick and H. J. Schönherr, *Chem. Ber.*, **103**, 1037 (1970).

(93) U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **6**, 805 (1967).

(93a) J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972).

(94) U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **6**, 560 (1967).

(95) U. Schöllkopf and F. Gerhart, *ibid.*, **6**, 970 (1967).



(10)

Related cyclic 2-oxycarbenes of platinum[88] and manganese[65] are almost certainly formed in similar ways.

C. SYNTHESES INVOLVING MODIFICATION OF A CARBENE LIGAND COORDINATED TO A METAL

The structures of the coordinated oxycarbene ligands of several group VI metal complexes (see Table I) bear noticeable similarity to carboxylic esters, *e.g.*, in C_{carb}–O and C_{acyl}–O bond lengths (see section II). This resemblance is also apparent in a number of reactions (see section IV.B): those with amines, acetaldehyde imine (see section IV.B.2), and thiols, *e.g.*, as illustrated in eq 11[45] and 12.[5] Such solvolyses, particularly with primary and secondary amines, have been widely used for preparing amino-carbene complexes, including those of binuclear manganese derivatives.[32] Reactions normally afford excellent yields, and products are easily separated.

$$(OC)_5CrC(OMe)Me + MeNH_2 \longrightarrow (OC)_5CrC(NHMe)Me + MeOH \quad (11)$$

$$(OC)_5CrC(OMe)Ph + PhSH \longrightarrow (OC)_5CrC(SPh)Ph + MeOH \quad (12)$$

Perhaps the most surprising syntheses of this type are those involving the enhanced acidity of α-hydrogen substituents of coordinated carbenes. The methyl groups of methylalkoxycarbene derivatives of Cr, Mo, and W exchange H with D from MeOD in a very fast reaction catalyzed by MeONa.[37] Not only have deuterated species been prepared in this manner, but using an equivalent of sodium alkoxide catalyst and trimethyloxonium tetrafluoroborate, one or two α-hydrogen atoms can be replaced by methyl groups;[36,37] this is illustrated in eq 13. The reaction has been found in the manganese series also,[5] where it has been cited as evidence for carbene structures,[65] as well as affording a route to deuterated species.

$$(OC)_5CrC(OMe)Me \xrightarrow[\text{equiv MeONa; 2. Me}_3\text{OBF}_4]{\text{1. THF, }-20^\circ} (OC)_5CrC(OMe)CH_nMe_{3-n} \quad (n = 1, 2, \text{or } 3) \quad (13)$$

$$(OC)_5CrC(OMe)Me \xrightarrow{\text{MeOD–MeONa}} (OC)_5CrC(OMe)CD_3$$

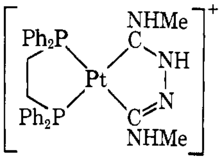
D. SYNTHESES INVOLVING LIGAND SUBSTITUTION OF A METAL CARBENE COMPLEX

The lability of carbonyl ligands is widely used in synthesis[96] and finds application in the preparation of phosphine-substituted compounds of Cr, Mo, and W, as illustrated in eq 14.[39] One triphenylphosphine molecule is displaced by CO from $(Ph_3P)_2ClRhC(NPhCH_2)_2$,[78] while Me_2PhP reacts with $(CO)Cl_3RhC(Ph)N(Me)C(Ph){=}NMe_2$ to give $(Me_2PhP)_2Cl_3RhC(Ph)N(Me)C(Ph){=}NMe$ and with $[(OC)Cl_3RhC(Me)NHC_6H_4Me\text{-}o]_n$ to give $(Me_2PhP)_2Cl_3RhC(Me)NHC_6H_4\text{-}Me\text{-}o$.[79]

$$(OC)_5CrC(OMe)Me + Bu^n{}_3P \longrightarrow cis\text{-}(Bu^n{}_3P)(OC)_4CrC(OMe)Me + CO \quad (14)$$

Isonitriles may be similarly displaced (eq 15) in the platinum series.[83] Anionic ligands may also be displaced; this has been demonstrated for platinum(II)[90] and palladium(II)[90] complexes [eq 16, M = Pd or Pt; L = $C(NPhCH_2)_2$, $C(NMeCH_2)_2$, or $C(NMe)C_6H_4S\text{-}o$]; the reaction proceeds more readily for cis than trans complex as is consistent with the higher trans-effect of carbene or R_3P than Cl^- (see sections II and V). Likewise, the chloride ligands in $(OC)Cl_3RhC(Ph)N(Et)C(Ph){=}NEt$ may be displaced by Br^- or I^-.[79]

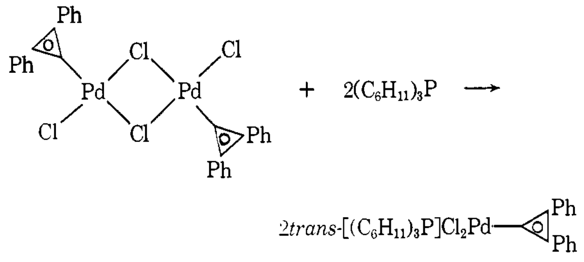
$$cis\text{-}[(MeNC)_2Pt(MeNHCNHN{=}CNHMe)]^+Cl^- + Ph_2PCH_2CH_2PPh_2 \longrightarrow$$



$$Cl^- + 2MeNC \quad (15)$$

$$(Et_3P)Cl_2ML \xrightarrow{\text{LiBr/Me}_2\text{CO}} (Et_3P)Br_2ML \quad (16)$$

The well-known nucleophilic cleavage of halogen-bridged compounds provides a route to a mononuclear palladium complex, as shown in eq 17.[84] Tin(II) chloride reacts normally (eq 18) with some Pd–Cl carbene complexes yielding compounds with metal–tin bonds.[85]



(17)

$$(PhNC)Cl_2Pd\text{-}C(NHPh)NHC_6H_4Me\text{-}p + 2SnCl_2 \longrightarrow trans\text{-}(PhNC)(Cl_3Sn)_2PdC(NHPh)(NHC_6H_4Me\text{-}p) \quad (18)$$

Some of these topics are considered further in Section IV, C.1.

E. SYNTHESES FROM SALT-LIKE PRECURSORS

The high heat of formation associated with many simple salts may result in an overall $-\Delta G_{\text{reaction}}$ for processes involving the preparation of relatively thermodynamically unstable products. Coupled with the insolubility of these by-products in common organic media making subsequent removal easier,

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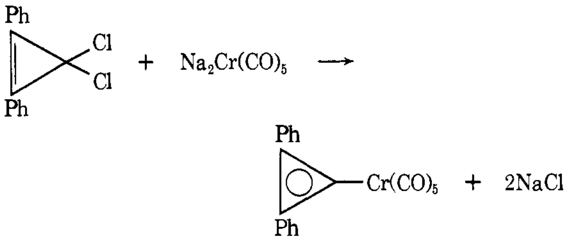
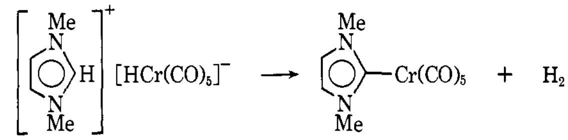
(96) P. Pino and I. Wender, "Organic Syntheses via Metal Carbonyls," Vol. 1, Interscience, New York, N. Y., 1968.

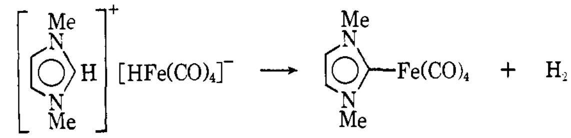
such reactions are often attractive synthetically. Examples where alternative syntheses are not to date available are in eq 19,[54] 20,[54] 21,[54] and 22.[91,92] Yields are not invariably high (see Table III).



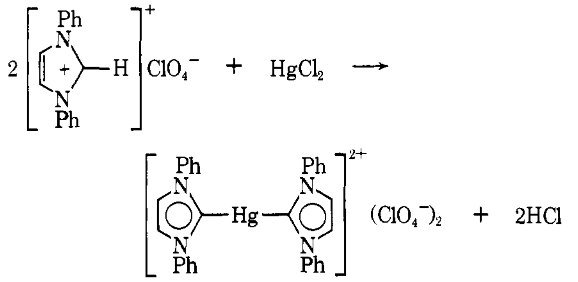
(19)



(20)



(21)

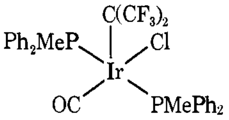


(22)

F. SYNTHESES FROM NEUTRAL CARBENE PRECURSORS

Although at first sight an obvious route, the trapping of carbenes on transition metals has proved notoriously difficult. While there is excellent evidence for the involvement of both metal and carbene (or precursor) in intermediates (see eq 23), the isolation of stable complexes has not proved possible until recently. For the two cases where evidence for carbene intermediates is good, the structures of the proposed complexes (**4**, **5**, and **6**) are not yet definitive. For those cases where the structures of the complexes is established [*e.g.*, *cis*- and *trans*-$(Et_3P)Cl_2PtC(NPhCH_2)_2$, Table I],[12,26] clear evidence for free carbene intermediates is not available (see below and section III.H).

It is well-established that carbene or substituted carbenes may be inserted into certain metal–X (X = H, Hal, etc.) bonds.[97] For the reaction of diazomethane with *trans*-$(Ph_3P)_2Ir(CO)Cl$ to afford *trans*-$(Ph_3P)_2Ir(CO)CH_2Cl$, a five-coordinate Ir–CH_2 intermediate was proposed.[81] With $(CF_3)_2CN_2$ and *trans*-$(Ph_2MeP)_2Ir(CO)Cl$, the balance of evidence (nmr) supported structure **4** rather than an isomeric insertion product into Ir–Cl.[80] The reaction of ethyl diazoacetate with cobalt(III) octaethylporphyrin has been explored and two complexes, formulated as **5** and **6**, have been isolated which were believed to have coordinated carbene ligands on the basis of analyses, spectroscopic data, and trapping experiments.[77] Definitive evidence for **4** to **6** would be especially welcome, as these formulas are unique at this time in having electrophilic carbene ligands. See Addendum.



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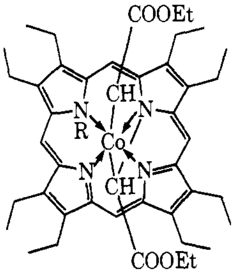
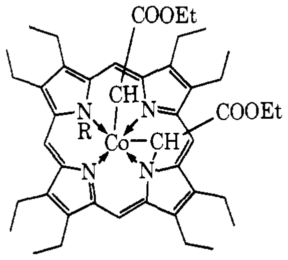


R = CH_2COOEt

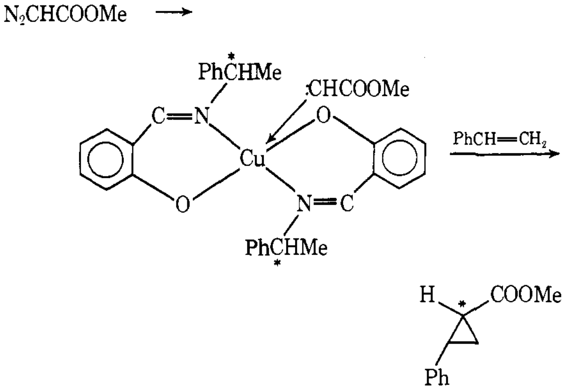
5



6

Difficulties have likewise been experienced in attempts to prepare transition metal complexes of other reactive intermediates. For example, it has not yet proved possible to trap benzynes on silver,[98] or plantinum,[99,100,101] although one such complex is known;[101a] this was prepared from $Os_3(CO)_{12}$ and triphenylphosphine in refluxing xylene.

An example of evidence for intermediates is the asymmetric synthesis of cyclopropanes from methyl diazoacetate, styrene, and an optically active catalyst (asymmetric center denoted with asterisks in eq 23).[102]



(23)

A number of reactions of electron-rich olefins[103,104] have led to trapping of carbene fragments.[12,78,86] Whether "free" carbenes are involved is not certain. At one time it was thought that electron-rich olefins, such as **7**, were in equilibrium with the corresponding nucleophilic carbene moieties; on balance,

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[97] M. F. Lappert and J. S. Poland, *Advan. Organometal. Chem.*, **9**, 397 (1970).

[98] L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967).

[99] H. J. S. Winkler and C. Wittig, *J. Org. Chem.*, 28, 1733 (1963).

[100] C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

[101] T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *Chem. Commun.*, 821 (1968).

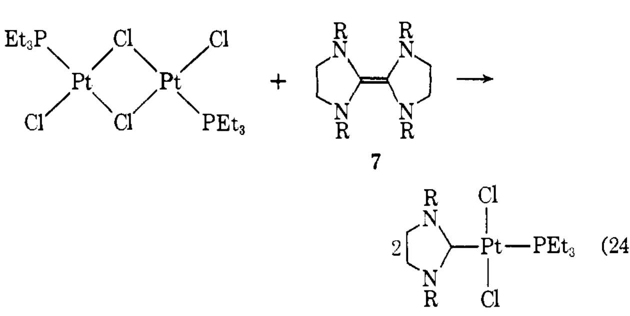
[101a] C. W. Bradford, J. M. Guss, G. Gainsford, P. Ireland, R. Mason, and R. S. Nyholm, *Pure Appl. Chem., Suppl.*, **6**, 31 (1971).

[102] H. Nozaki, S. Moriati, H. Takaya, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

[103] R. W. Hofmann, *Angew. Chem., Int. Ed. Engl.*, 7, 754 (1968).

[104] N. Wiberg, *ibid.*, 7, 766 (1968).

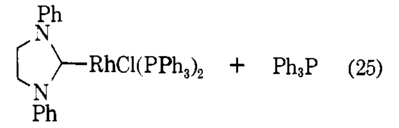
present evidence does not support this hypothesis.[103] The nucleophilicity of the carbenes formally derived from bis-(1,3-diphenylimidazolidinylidene-2) (**7**, R = Ph), and related electron-rich olefins, suggested that transition metal complexes known to be susceptible to nucleophilic attack might form suitable "carbene traps." The first carbene complex, **8** (R = Ph), prepared in this way is shown in eq 24.[12]



(24)

This reaction, which is normally carried out in refluxing xylene, has been generalized (see Table III): other electron-rich olefins which have been used are **7** (R = Me) and **9**, and transition metal bridged substrates include $(Et_3P)_2X_4M_2$ (X = Cl or Br, and M = Pd or Pt),[86] $(Ph_3P)_4Cl_2Rh_2$,[78] and $(Ph_3P)_2(OC)_2Cl_2Rh_2$.[78] Reactivity decreases in the order **7** (R = Me) > **7** (R = Ph) ≈ **9**, and Pd > Pt.[86] The olefin sequence thus broadly parallels "electron-richness," the compounds have exceptionally low first ionization potential [*e. g.*, 6.05 eV for 7 (R = Me)],[105] as shown by photoelectron spectroscopy, while the substrate order is consistent with their general susceptibility to nucleophilic attack. Halide-bridging is clearly not a limiting criterion, as shown in eq 25;[78] another suitable substrate is $(Ph_3P)_2(OC)ClRh$.

$(Ph_3P)_3RhCl + {}^1/_2\ 7\ (R = Ph) \longrightarrow$



$+ Ph_3P$ (25)

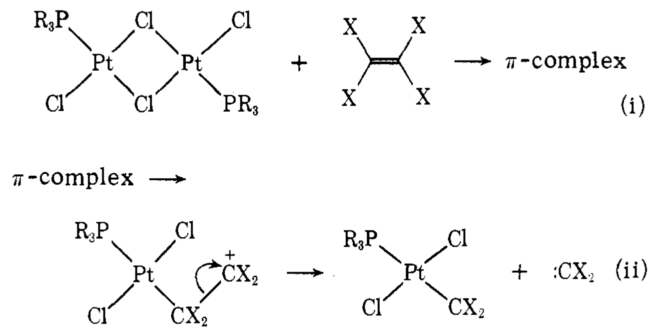
The yields in these reactions are usually high, and subsequent work-up is straightforward (particularly with the bridge splitting reactions where there are no other products). Whether the reactions are bimolecular or involve predissociation of the olefin is not known. The trichloromethyl derivative **10** is also effective in place of the electron-rich olefin (R = Ph) for the preparation of carbene complexes as in reaction 24, but is it known that **10** affords the olefin in hot xylene;[103] and coordination of olefin seems a plausible initial step, as shown in Scheme I.

There is no direct evidence for the participation of free carbene in the platinum series. Scheme II shows displacement of carbene using an electron-rich olefin in a rhodium(I) system.[78]

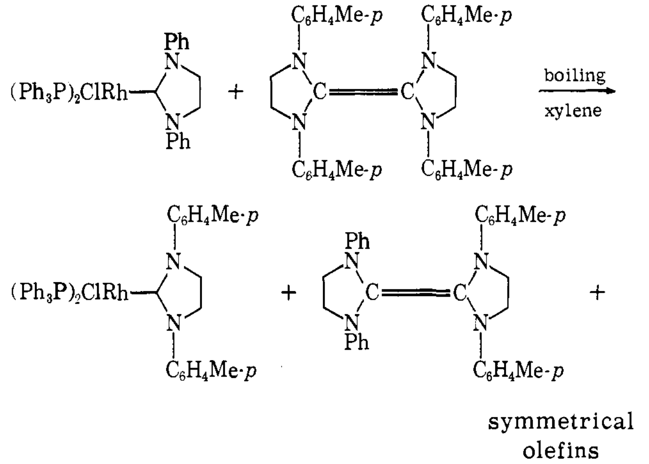
The product of reaction 24 is the trans compound, but in other cases the reaction is not stereospecific, because trans carbene complexes of Pd(II) and Pt(II) undergo isomerization upon heating (see section III.I).

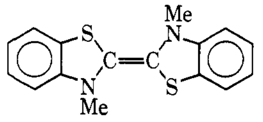
The reaction of a thioketocarbene with $Fe(CO)_5$ affords

Scheme I



Scheme II





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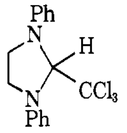

10

a binuclear complex in which the carbene is bound in a delocalized π system (see Table III).[19] Further examples of this type of synthesis have not been reported.

G. SYNTHESES INVOLVING OXIDATIVE ADDITION

In principle, the synthesis of a metal–carbene complex in which the metal is in a relatively high oxidation state may be achieved by an oxidative addition reaction involving three fragments adding to a coordinatively unsaturated low-oxidation-state metal substrate. Such reactions have recently been realized for a number of rhodium(III) compounds and for the addition of 3,3-dichloro-1,2-diphenylcyclopropene to metallic palladium (see Table III). Two different types of reaction paths have been found, illustrated in eq 26 and 27, for reactions of imidoyl halides with suitable rhodium(I) substrates.[79]

The mechanism of such reactions is not yet clear. Presumably the ligand coupling reaction to give compounds such as **11** occurs on the metal, with the latter acting as template. Likewise, it is not yet clear whether or not hydrogen chloride

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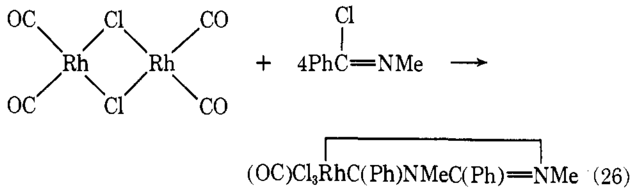
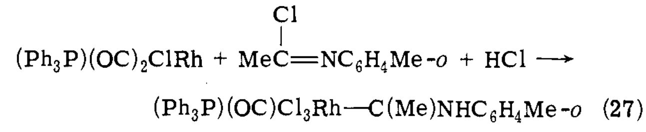
(105) B. Çetinkaya, G. H. King, S. S. Krishamurthy, M. F. Lappert, and J. P. Pedley, *Chem. Commun.*, 1370 (1971).



$$(OC)Cl_3RhC(Ph)NMeC(Ph){=}NMe \quad (26)$$

11



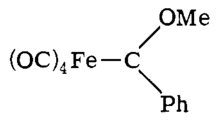
$$(Ph_3P)(OC)_2ClRh + MeC(Cl){=}NC_6H_4Me\text{-}o + HCl \longrightarrow (Ph_3P)(OC)Cl_3Rh{-}C(Me)NHC_6H_4Me\text{-}o \quad (27)$$

12

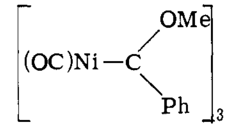
and the imidoyl chloride, in reactions such as that shown in eq 27 to afford **12**, interact within the coordination sphere of the metal.

H. CARBENE TRANSFER REACTIONS

Only two papers relate to the successful intermetallic transfer of a carbene ligand.[56,58] Among the compounds prepared were **13** and **14**. The former could not be obtained by the conventional organolithium route, and **14** is the only presently known carbene complex of nickel.



13



14

It seems likely that if carbenes are intermediates, their high reactivity is likely to restrict the application of the method. However, it is not inevitable that such intermediates are involved and kinetic data are not available. See section VII.

Some of the isomerization reactions described in section III.I may belong to this reaction type.

I. ISOMERIZATION REACTIONS

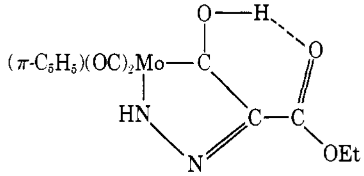
At this time two types of isomerizations are known for carbene complexes: those which involve rearrangement of the ligands in the coordination sphere of the metal, and those in which two rotamers are interconverted by rearrangement within an aminocarbene ligand.

For the square-planar Pd(II) and Pt(II) carbene (L) complexes $(R_3P)X_2ML$ [M = Pd or Pt; X = Cl or Br; L = $C(NPhCH_2)_2$, $C(NMeCH_2)_2$, or $C(NMe)C_6H_4S\text{-}o$] it has been shown that the cis isomers are thermodynamically the more stable, being obtained from the trans compounds by heating.[90] This was first demonstrated for **8**, which melts initially at 210–205° and resolidifies, finally melting at 315–318° dec; the cis isomer is formed below 250°.[26,90] Such thermal isomerizations among square-planar platinum(II) complexes are well known, but not usually in the sense trans → cis (see, ref 116a). Another method of isomerization involves heating in refluxing alcohol (EtOH but not MeOH for **8**, but MeOH for the Pd analog). The reacivity sequences with respect to ease of isomerizations of such trans complexes are Pd >Pt and $C[N(Me)CH_2]_2 \approx C[N(Me)C_6H_4S\text{-}o] > C[N(Ph)CH_2]_2$.[90] Thus, for the reaction type shown in eq 24, under identical conditions (heating in xylene), the olefins **7** (R = Me) and **9** gave cis/trans mixtures of carbene products, whereas **7** (R = Ph) stereospecifically afforded the trans complex **8**. The trans complexes thus owe their preparation to kinetic rather than thermodynamic factors. Further nonpreparative aspects are discussed in section IV.B.2.

As mentioned in section II, and discussed elsewhere (sections IV.B.1, IV.B.2, and V), aminocarbene-metal complexes may exist in isomeric forms distinguished by different orientations of substituents about the C_{carb}–N bond, rotation about which is restricted. For complexes such as $(OC)_5MC(R)NHR^1$ or $(R^2{}_3P)(OC)_4MC(R)NHR^1$ (M = Cr, Mo, or W), cis compounds (*i.e.*, those having M and H on the same side of the C_{carb}–N bond) may be coverted (see section IV.B.1) into trans isomers, and the reaction is base catalyzed.[63,106,107]

J. MISCELLANEOUS SYNTHESES

A number of curious carbene products are listed under this heading (method J) in Table III. These are a Cr–isonitril-adduct,[29,29a] derivatives of Mo,[59] Mn,[65–67] and Pt[88] with the carbene ligand-$C(CH_2)_3O$ (see eq 10), thio compounds of Mn[64] and Fe[19] (see section III.F), and the interesting Mo complex **15**.[61,62] This was obtained unexpectedly from Na[(π-C_5H_5)(OC)$_3$Mo] and diazoacetic ester; here, the carbene carbon is presumably not the "potential-carbene" atom of the diazo compound, but rather is derived from a CO molecule perhaps in a manner similar to that shown in eq 10.



15

IV. Reactions of Carbene Complexes

A. INTRODUCTION

The carbene complexes vary widely in reactivity, from highly reactive carbonyl derivatives of the group VI and VII metals (and iron) to some rather unreactive platinum compounds. Here both types of complex will be treated together and the discussion divided according to reaction type. The reactions have been classified broadly into two headings: (i) reactions in which the carbene ligand is modified; often remaining a carbene complex, but always with the elements of the carbene moiety retained in the metal coordination sphere (section IV.B), and (ii) reactions in which the ligand is lost from the metal complex, either by displacement or in a decomposition reaction (section IV.C). For reactions of type i, there is clearly some overlap with material discussed in sections III.D and III.I.

B. REACTIONS IN WHICH THE CARBENE IS MODIFIED

1. Reactions with Ammonia, Amines, and Related Compounds

The reactions of the carbene complexes of Cr, Mo, and W, with ammonia, and primary and secondary amines were dis-

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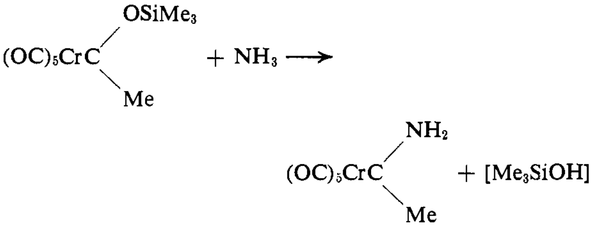
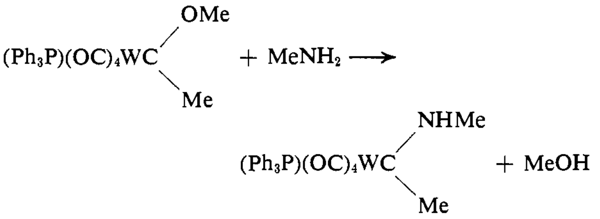
(106) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **15**, 147 (1968).

(107) C. G. Kreiter and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **8**, 761 (1969).

covered shortly after the preparation of the first carbene complexes by Fischer and his coworkers.[45] The synthetic use of these reactions has been emphasized (section III.C), and eq 11 is a typical example. Their generality is considerable (see Table III), and extensions have been made to siloxycarbenes (eq 28),[30] phosphine-substituted complexes (eq 29),[63] and other metals [*e.g.*, eq 30).[32]



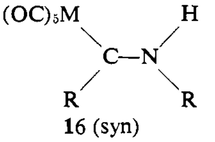
$$(OC)_5CrC(OSiMe_3)Me + NH_3 \longrightarrow (OC)_5CrC(NH_2)Me + [Me_3SiOH] \quad (28)$$



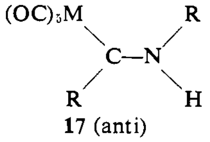
$$(Ph_3P)(OC)_4WC(OMe)Me + MeNH_2 \longrightarrow (Ph_3P)(OC)_4WC(NHMe)Me + MeOH \quad (29)$$

$$(OC)_5MnMn(CO)_4C(OMe)Me + NH_3 \longrightarrow (OC)_5MnMn(CO)_4C(NH_2)Me + MeOH \quad (30)$$

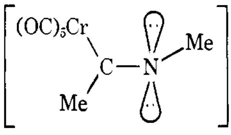
Aminocarbene complexes (and alkoxycarbene complexes) can exist in syn-anti isomeric forms about the "double bond" of the carbene ligand (**16** and **17**). The isomers are not only stable in the solid state, but spectroscopic evidence is available (section V) for their independent existence in solution. In the aminolysis reactions, the products have the syn configuration. The phosphine-tetracarbonyl complexes (eq 29) have the syn structure initially, but the pentacarbonyl derivatives which can be isomerized (see also section III.I) to the anti configuration [completely for W compounds, partially for the Cr derivatives], afford *syn*-aminocarbenes. The configuration of the starting materials appears not to be significant.[63] In the presence of *tert*-butyl alcohol and butoxide, the syn tungsten pentacarbonyl product is converted entirely into the anti isomer, but the phosphine derivative affords a syn:anti 1:3 mixture. The phosphine-chromium product is not isomerized under these conditions. The pentacarbonylchromium derivative behaves differently. Aminolysis with methylamine affords only the syn aminocarbene, but KOH brings about partial rearrangement to the anti configuration in about 0.5 hr at room temperature.[106] Methanolic KOH yields a 5:4 anti:syn mixture which undergoes no further change during 40 hr. Sodium methoxide affords a similar product ratio, but butoxide converts the amino compound substantially to anti (anti:syn 10:1). Addition of butoxide to the pure anti isomer affords the same mixture, and the position of equilibrium is evidently base dependent. The mechanism of rearrangement probably involves proton abstraction by the base, forming intermediates of type **18**, which subsequently may yield either isomer. Such a mechanism parallels that suggested for rearrangement of Schiff's bases and related compounds.



16 (syn)



17 (anti)



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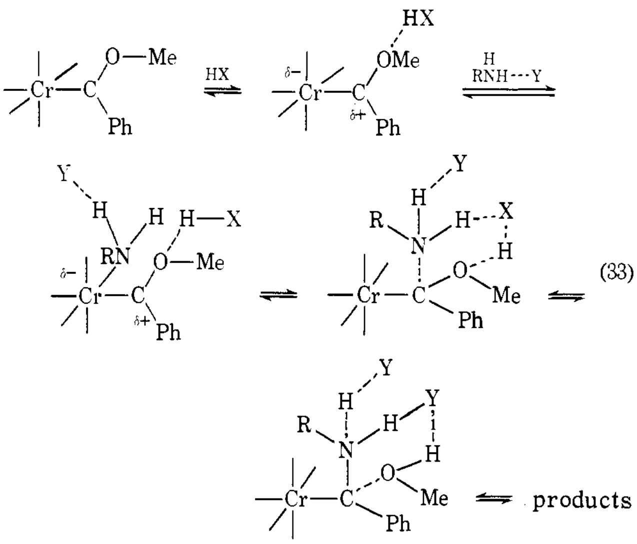
The mechanism of aminolysis has been studied in detail spectrophotometrically for reactions 31;[108,109] the rate law is given by eq 32. In eq 32, HX is a proton-donating and Y a proton-accepting species. The proposed mechanism is shown in eq 33. In *n*-decane, the amine itself must provide both HX and Y, and the observed rate follows eq 34, whereas in dioxane, which can act as a proton acceptor (role of Y), the rate expression becomes eq 35 (under pseudo-first-order conditions).

$$(CO)_5CrC(OMe)Ph + RNH_2 \longrightarrow (OC)_5CrC(NHR)Ph + MeOH \quad (31)$$

19: λ_{max} 406 nm (hexane)

20: λ_{max} 362-366 nm (hexane)

$$d[\mathbf{20}]/dt = k_n[\mathbf{19}][RNH_2][HX][Y] \quad (32)$$



(33)

$$d[\mathbf{20}]/dt = k[\mathbf{19}][RNH_2]^3 \quad (34)$$

$$d[\mathbf{20}]/dt = k^1[\mathbf{19}][RNH_2]^2 \quad (35)$$

Spectroscopic evidence for the hydrogen bonding with HX has been found. By assuming that the proton transfer from RNH_2 to Y is immediately after, or even synchronous with, the formation of the carbon-nitrogen bond, it is possible to account for the unusual temperature dependence (negative activation energy) of the reaction.[109]

Tertiary amines, *e.g.*, pyridine, by contrast displace the carbene ligand (see section IV.C). The only thiol reaction known is described in section III.C. Reactions with cyclic secondary amines are described in ref 43b.

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(108) B. Heckl, H. Werner, and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, 7, 817 (1968).

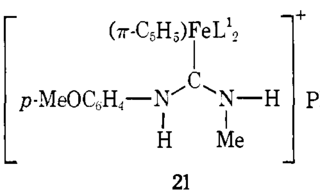
(109) H. Werner, E. O. Fischer, B. Heckl, and C. G. Kreiter, *J. Organometal. Chem.*, 28, 367 (1971).

2. Isomerizations

As discussed in section III.D, there are two aspects to this problem. For the palladium(II) and platinum(II) $(Et_3P)X_2ML$ complexes, the thermal isomerizations trans → cis are noteworthy.[26,90] For other square-planar Pd(II) and Pt(II) complexes, the reverse isomerizations are well known and are induced thermally, photochemically, or by addition of base, while trans → cis isomerizations are rare. For these cis and trans Pd(II) and Pt(II) carbene complexes (see Table III) there are differences in (i) color (cis are white and trans yellow), (ii) melting point (cis > trans), (iii) solubility in nonpolar solvents (trans > cis), (iv) $\nu(PtX_2)$ far-ir characteristics (X = Cl), both in number of strong bands (cis > trans) and position (trans > cis, in energy), (v) magnitudes of $J(^{195}Pt-P)$ (cis > trans), (vi) reactivity of chloride to displacement by bromide (cis > trans) (see section III.D), and (vii) thermodynamic stability (cis > trans).

As mentioned in section IV.B.1, the restricted rotation about the C_{carb}–N bond of aminocarbenes is revealed by the existence of cis–trans isomers. Some aminocarbenechromium compounds have been separated, and the isomers differ in melting point and solubility. The ^1H nmr spectrum of $(OC)_5CrC(OMe)Ph$, which was originally thought to show the presence of only one isomer, has now revealed both in acetone-d_6 at −40°. Details are in section V. As with aminocarbene complexes, rearrangement of this alkoxycarbene requires a base catalyst.[107]

For bis(amino)carbenecyclopentadienyliron(II) compounds, restricted rotation about each C_{carb}–N bond leads to a total of four possible isomers, of which two are shown in **21** and **22** (L^1 = $p-MeOC_6H_4NC$).[70] Furthermore, if the rotational barrier in the Fe–C bond were high enough, each could exist in a cis or trans arrangement of cyclopentadienyl ring and (say) the NHMe group about the metal. Restricted rotation about a C_{carb}–N bond in an iron complex has been observed in $(\pi-C_5H_5)(OC)(MeNC)FeC(=NMe)C_6F_5$.[110] However, in this case only two isomers could be distinguished, and they were tentatively assigned structures similar to **21** and **22**, of which the former was thought to be the predominant species (ratio **21**:**22**, 1.6:1). The isomers equilibrate relatively rapidly, unlike the chromium compounds described above.



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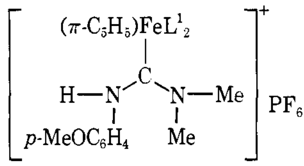


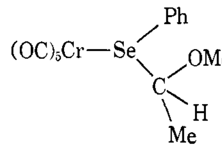
22

3. Deuterium Exchange and Metalation Reactions

These have been described in section III.C.

4. Insertion Reaction with Selenophenol

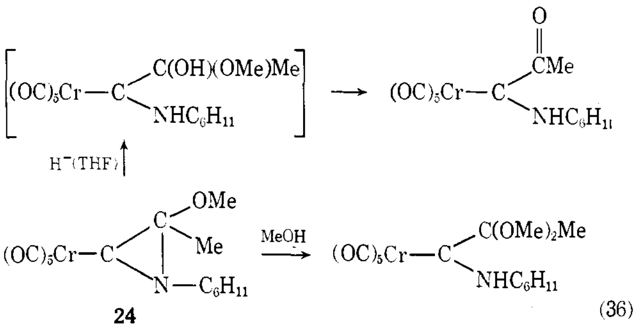
The reaction of $(OC)_5CrC(OMe)Me$ with PhSeH is surprising. No methanol is liberated, and the selenoether complex **23** is formed.[50] This is thus one of a few examples where a reagent might be regarded as having added to a metal=C_{carb} double bond; it is then necessary to postulate subsequent insertion of the SePh group into the Cr–C bond. By analogy with reactions described in section IV.B.1, a selenocarbene complex $(OC)_5CrC(SePh)Me$ might have been expected. Compound **23** shows a parent ion (*m/e* 406 and 408) in the mass spectrum, and the presence of Me, OMe, CH, and Ph groups is established from the ^1H nmr spectrum. The selenoether ligand PhSeC(OMe)CHMe can be replaced by pyridine. The molybdenum and tungsten analogs behave similarly. In ethanol, $(OC)_5CrC(OMe)Me$ reacts with PhSeH to form a red oil from which a crystalline solid is precipitated by strong, aqueous KOH. This is believed to be $K^+[(OC)_5CrSe(Ph)Cr(CO)_5]^-$.[50]



23

5. Insertion Reaction with Cyclohexyl Isocyanide

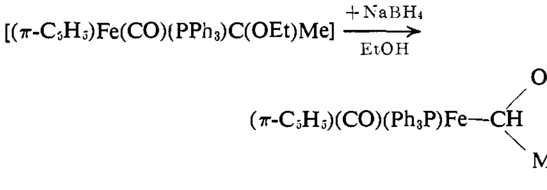
The reaction of $(OC)_5CrC(OMe)Me$ with cyclohexyl isocyanide initially affords a yellow 1:1 adduct which is very sensitive to light and air and is instantly decomposed by acids. The aziridine structure **24** for this complex has been established spectroscopically and by the interesting reactions shown in eq 36;[29a,49] benzoyl peroxide also reacts with **24**.



(36)

6. Reduction

One example (eq 37) is known in which a coordinated carbene is reduced to a substituted methyl compound.[60] Treatment of $(OC)_5CrC(OMe)Me$ with $Li[AlH(OBu^t)_3]$ in THF at 20° provided $(OC)_5CrC(OMe)CH=CHCH=C(OMe)Me$ in less than 0.1% yield.[42]



$$[(\pi-C_5H_5)Fe(CO)(PPh_3)C(OEt)Me] \xrightarrow[EtOH]{+NaBH_4} (\pi-C_5H_5)(CO)(Ph_3P)Fe-CH(OEt)Me \quad (37)$$

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(110) P. M. Treichel and J. P. Stenson, *Inorg. Chem.*, 8, 2563 (1969).

Attempts to reduce carbene complexes of the group VI metals with a variety of reducing agents (including dissolving metals or complex hydrides) led either to complete decomposition or gave no reaction.[111] The difficulty with such experiments, or their retrogressions, is that an oxidation state change of unity is involved. Where a particular transition metal forms organometallic compounds in more than one oxidation state, these normally differ by units of two, *e.g.*, Pt(II) and Pt(IV). For hydrogen transfer experiments to be successful, it is therefore likely that they must be intramolecular.

C. REACTIONS IN WHICH THE CARBENE OR ANOTHER LIGAND IS DISPLACED

1. *Reactions with Phosphorus Derivatives*

A variety of alkyl-, aryl-, and (alkyl)aryl-phosphines and phosphites react with pentacarbonylcarbene derivatives of Cr, Mo, and W affording the cis ligand–carbene tetracarbonyl derivatives.[39] Traces of phosphinepentacarbonyl and bis(phosphine)tetracarbonyl compounds (<5%) are also produced. A kinetic study[41] has shown a two-term rate law involving parallel dissociative (−CO) and associative mechanisms, the relative proportion of which is dependent upon the ligand. The halides PI_3 and PBr_3 by contrast afford the compounds $(OC)_5MPX_3$ (M = Cr, Mo, W), which were the first transition metal complexes of these ligands to be prepared.[112] (For the preparation of these complexes, it is not necessary to isolate the carbene intermediates.) Phosphine itself behaves differently again, as shown in eq 38.[113] The product has the cis configuration, and the eliminated "carbene" fragment rearranges by a hydrogen migration and is isolated as vinyl methyl ether.

$$(OC)_5CrC(OMe)Me + 2PH_3 \longrightarrow (OC)_4Cr(PH_3)_2 \quad (38)$$

With tertiary phosphines, the Chugaev-salt carbene types behave analogously to the group VI metal compounds, affording phosphineplatinum carbene complexes.[83] From the bisisonitrile compounds, the isonitrile ligands are replaced by bis(diphenylphosphino)ethane giving the new salts $[Pt(C_4H_9N_4)diphos]^+Cl^-$. Other examples of displacement reactions both of neutral (such as CO or R_3P) and anionic (Cl^-) ligands have been described in section III.D. With some rhodium(I) complexes, the carbene ligand may also be displaced, as in eq 39 and 40.[78]

$$(Ph_3P)(OC)ClRhC(NPhCH_2)_2 \xrightarrow{PPh_3} (Ph_3P)_2(OC)ClRh \quad (39)$$

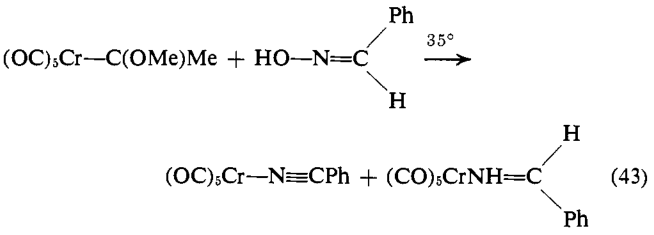
$$(Ph_3P)_2ClRhC(NPhCH_2)_2 \xrightarrow{Ph_2PCH_2CH_2PPh_2} [(Ph_2PCH_2CH_2PPh_2)_2Rh]Cl \quad (40)$$

2. *Reactions with Nitrogen Derivatives: Hydrazines, Oximes, Hydroxylamine, and Tertiary Amines*

Whereas primary and secondary amines react with carbene complexes of Cr, Mo, and W, affording new amino-carbene derivatives (see also section III.C), tertiary amines displace the carbene ligand [*e.g.*, eq 41, py = C_5H_5N].[48] The ratio of products depends on the conditions of the reaction. Hydroxylamine affords complexes in which the elements of the carbene ligand are not lost, as shown in eq 42. Both cis and trans isomers are produced, which are interconverted in an equilibrium whose temperature dependence has been studied.[52] Oximes, however, can afford a variety of products, as shown in eq 43.[51] By gentle warming of the reaction mixture, to prevent decomposition of the intermediate carbene complex $[(OC)_5CrC(N{=}CHPh)Me]$, only traces of the benzonitrile adduct are obtained. Carbene analogs are also produced from $PhMeC{=}NOH$ and $Ph_2C{=}NOH$. In these complexes only one of the cis–trans isomers is formed, and the ^1H nmr evidence suggests that it is the trans derivative.

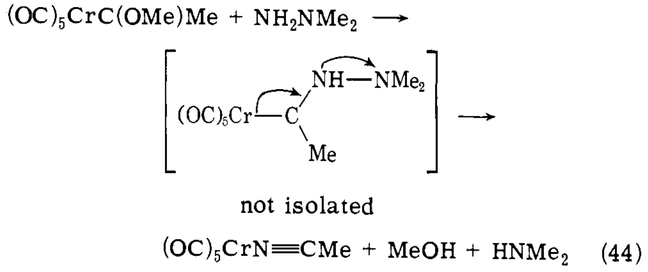
$$(OC)_5CrC(OMe)Ph + py \longrightarrow pyCr(CO)_5 + cis\text{-}(py)_2Cr(CO)_4 \quad (41)$$

$$(OC)_5CrC(OMe)Me + NH_2OH \longrightarrow (OC)_5CrNH{=}C(OMe)Me + H_2O \quad (42)$$



$$(OC)_5Cr{-}C(OMe)Me + HO{-}N{=}C(Ph)H \xrightarrow{35^\circ} (OC)_5Cr{-}N{\equiv}CPh + (CO)_5CrNH{=}C(H)Ph \quad (43)$$

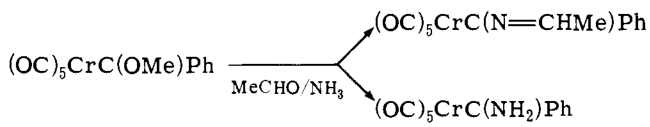
Substituted hydrazines yield nitrile complexes, but it is probable that an unstable carbene is initially produced. A possible route is suggested in eq 44. It is interesting that the salt $Me_4N[(OC)_5CrC(O)CH_2SiMe_3]$ with HN_3 affords both $MeNCCr(CO)_5$ and $MeCNCr(CO)_5$, but the reaction mechanism is not yet known.[44a]



$$(OC)_5CrC(OMe)Me + NH_2NMe_2 \longrightarrow \left[(OC)_5Cr{-}C(Me)NH{-}NMe_2\right] \longrightarrow (OC)_5CrN{\equiv}CMe + MeOH + HNMe_2 \quad (44)$$

not isolated

With acetaldehyde imine, or more strictly the acetaldehyde-ammonia adduct ($MeCHO + NH_3 \rightleftharpoons MeCH(OH)NH_2 \rightleftharpoons MeCH{=}NH + H_2O$), an imino carbene was isolated in low yield (eq 45).[55]



$$(OC)_5CrC(OMe)Ph \xrightarrow{MeCHO/NH_3} (OC)_5CrC(N{=}CHMe)Ph + (OC)_5CrC(NH_2)Ph \quad (45)$$

3. *Reactions with Miscellaneous Reagents*

The carbene is cleaved from the group VI metal complexes by mineral acids. Hydrogen iodide reacts with the chromium compounds to form an iodide-bridged binuclear chromium ion which may be isolated (eq 46) as a quaternary ammonium

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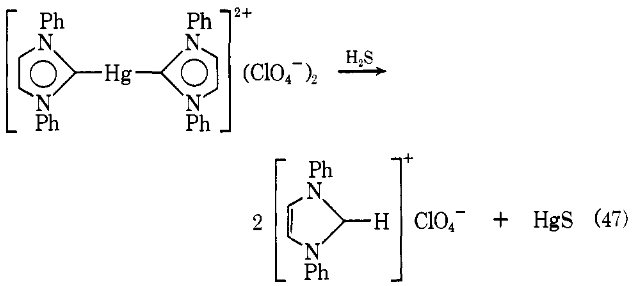
[111] D. J. Cardin, B. Çetinkaya, and M. F. Lappert, unpublished observations.

[112] E. O. Fischer and L. Knauss, *Chem. Ber.*, 102, 223 (1969).

[113] E. O. Fischer, E. Louis, W. Bathelt, E. Moser, and J. Müller, *J. Organometal. Chem.*, 14, P9 (1968).

$$(OC)_5CrC(OMe)Me + HI \xrightarrow[(Me_4N^+)(H_2O)]{(ether)} [(OC)_5CrICr(CO)_5]^-NMe_4^+ \quad (46)$$

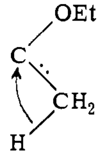
salt.[5] The Chugaev-salt carbenes react with mineral acids by protonation of a carbene-nitrogen atom forming the appropriate dication,[83] without cleavage of the carbene. The phosphinedihalogenoplatinum carbenes do not react with mineral acids.[114] For further reactions of cis and trans carbene complexes of platinum and palladium, see ref 90, and sections III.D, III.I, and IV.B.2). Similar carbene derivatives of mercury, however, are decomposed by hydrogen sulfide (eq 47);[91] the metal-carbene complex may be re-formed using mercuric acetate in dimethyl sulfoxide.



(47)

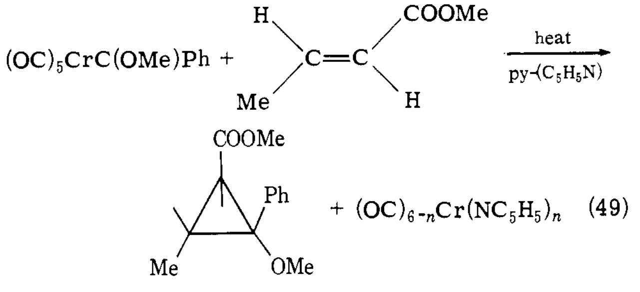
4. Reactions of Displaced Carbene Fragments

Evidence for carbene intermediates has often been sought in trapping experiments with suitable olefins, *e.g.*, with cyclohexene to form norcarane derivatives.[115] Displacement of carbene from $(OC)_5CrC(OEt)Me$ can be achieved by reaction with carbon monoxide at 80° in an autoclave.[116] When this reaction is carried out in the presence of cyclohexene, none of the expected bicyclic compound is observed. Instead, the carbene rearranges by a hydrogen migration i and formation of ethyl vinyl ether. The same process intervenes in the thermal decomposition of carbene complexes with pyridine in the presence of cyclohexene. Furthermore, the presence of the base is not necessary for the hydrogen migration reaction. In the presence of tetramethylethylene as a carbene trap, either with base or by heating alone, carbene dimerization has been observed (eq 48).[117] The cis/trans ratio of the product stilbenes is strongly dependent on the experimental procedure employed. A further interesting observation is the presence of traces of α,α-dimethoxystilbene, from thermal decomposition experiments, but the significance of this is not yet clear. Whether these reactions involve free carbenes remains to be established. The carbenes have been trapped by olefin, however, by use (eq 49) of *trans*-methyl crotonate;[118] the configuration of the substituted cyclopropane was established from nmr spectra.



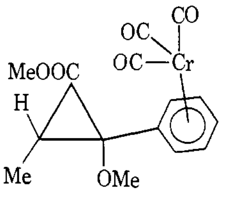
i

$$2(OC)_5CrC(OMe)Ph \longrightarrow cis\text{-} + trans\text{-}Ph(MeO)C{=}C(OMe)Ph \quad (48)$$



(49)

Also produced in the thermal reaction of the carbene complex with the olefin were small quantities of **25**, the metal-π arene derivative of the cyclopropane.[118] It is interesting to note that the thermal decomposition of $(OC)_5CrC(NMe_2)Ph$ afforded $Me_2NCHPhCHPhNMe_2Cr(CO)_4$ rather than the olefin.[119]



25

Since known carbene-metal complexes are those of nucleophilic carbenes, the use of simple olefins as traps is clearly not appropriate; compounds such as cyclohexene are suitable for electrophilic carbenes. Electron-withdrawing substituents on the olefin are desirable and diethyl fumarate should be an appropriate reagent.

A further example of carbene trapping using triethylsilane is interesting.[119] In this case the carbene fragment inserts into the Si-H bond. Such traps may be of more general utility for reactions in which nucleophilic carbenes are present, but *trans*-$(Et_3P)Cl_2PtC(NMeCH_2)_2$ with Et_3SiH affords *trans*-$(Et_3P)(Cl)(H)PtC(NMeCH_2)_2$.[90]

V. Spectroscopic Properties

A. INTRODUCTION

Until now there has been no direct spectroscopic probe for the presence of a coordinated carbene analogous, say, to the characteristic nmr signals exhibited by transition metal hydride complexes. The recently reported ^{13}C nmr shifts of C_{carb} atoms may provide such a tool (see section V.C.3). Nevertheless, spectral correlations have provided much information about structures (see section V.B.1), activation parameters for interconversion of rotamers (see section V.B.2), and electronic aspects (see section V.C) of carbene complexes. These points are illustrated by some examples: aminocarbenechromium complexes, π-arenecarbenedicarbonylchromium compounds,

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(114) E. M. Badley, D. Phil. Thesis, University of Sussex, 1969.

(115) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Arynes," Nelson, London, 1969, Chapter 5.

(116) E. O. Fischer and A. Maasböl, *J. Organometal. Chem.*, 12, P15 (1968).

(116a) E. A. Allen and N. P. Johnson, *Chem. Commun.*, 171 (1971).

(117) E. O. Fischer, B. Heckl, K. H. Dötz, J. Müller, and H. Werner, *J. Organometal. Chem.*, 16, P29 (1969).

(118) E. O. Fischer and K. H. Dötz, *Chem. Ber.*, 103, 1273 (1970).

(119) J. A. Connor and P. D. Rose, *J. Organometal. Chem.*, 24, C45 (1970); J. A. Connor, and J. P. Lloyd, *J. Chem. Soc. A*, 3237 (1970).

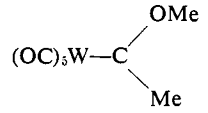
$(OC)_5WC(OMe)Me$, $(OC)_9Mn_2C(OMe)R$, and some Pd(II) and Pt(II) complexes including Chugaev salts. For convenience, electric dipole moment data are also discussed in section V.C.1.

Mass spectra have proved useful analytically, when parent molecular ions are present (see footnote on spectral details to Table III). Only one full paper is devoted to mass spectrometric studies (of Cr),[120] and ionization potentials are considered in section V.C.1. A common feature of fragmentation patterns is that ions containing both metal and carbene are present in high abundance.

B. STRUCTURAL DATA

1. General Considerations

The structural assignment of the first reported carbene complex, $(OC)_5WC(OMe)Me$ for which either the carbene (**26**) or acyl (**27**) formulation was plausible, was based on ir and nmr data.[4] There are no absorptions in the range 1500–1800 cm^{-1}, which could correspond to the acyl ν(CO) band of **27**. The ^{1}H nmr spectrum shows two singlets of equal intensity at τ 6.17 and 7.69 assigned respectively to the C-Me and C-OMe protons of **26**; the lack of absorptions to higher field excludes the W-Me grouping of **27**.[27] [The W-Me group of $(\pi\text{-}C_5H_5)(OC)_3WMe$ is found at τ 9.55.[4]] The ir band assignments are at 1250 ν(C-O), 1019 $\nu(H_3C\text{-}O)$, 893 ν(C-C), and 281 cm^{-1} ν(W-C), fully consistent with **26**, conclusions which were confirmed by an X-ray structural analysis (see section II).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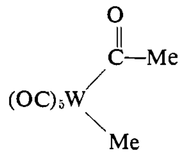
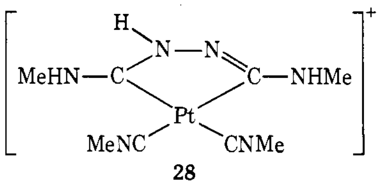

27

The question of whether an axial or equatorial carbene group is present in $(OC)_9Mn_2C(OMe)R$ has been studied by ir spectroscopy.[32] The phenyl derivative (R = Ph) has the former configuration [five ir-active ν(CO) bands], and the methyl (R = Me) the latter [nine ir-active ν(CO) bands expected from group theory].

The re-formulation of the Chugaev compounds as carbene complexes relied heavily on ^{1}H nmr spectroscopy.[2] The absorptions at τ 7.22 (6) and 6.69 (6) of the tetraphenylborate salt recorded in acetone-d_6 (relative intensities in parentheses) were assigned to the N-Me groups in **28**. In nitrobenzene, these absorptions occur at τ 7.08 (a symmetrical doublet with J(HH) = 5 Hz, assigned to the N-Me groups of the heterocycle) and 6.50 [a singlet, not present in the spectrum of $Pt(C_4H_9N_4)(diphos)BPh_4$, and assigned to the coordinated isonitrile ligands]. Deuteration using excess D_2O removes the J(HH) coupling, indicating the MeNH environment of the methyl groups. Addition of CF_3COOH, which inhibits exchange of NH protons, restores the J(HH) coupling in the diphosphine complex. The broad band at τ 4–5 in these compounds disappears on deuteration and is due to the NH protons, while experiments, using known quantities of D_2O by integration of HDO with respect to N-Me signals, showed that there were three NH protons. Other evidence, notably from ir spectroscopy, led to the formulation **28**, which receives further support from the X-ray structure analysis of a related Pd complex.[3]


28

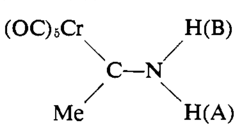
The cis square-planar dichloroplatinum(II) and-palladium(II) carbene complexes (see ref 12, 14, 86, 90) show the expected two $\nu(MCl_2)$ stretching modes. In a number of cases assignments have been confirmed by replacement of chloride with bromide (see, *e.g.*, ref 90). The trans derivatives generally show a single strong absorption in the metal–halogen stretching region.

^{1}H nmr spectra of the complexes $\{PtX[C(NHR)Q](PEt_3)_2\}^+ClO_4^-$ (see Table III) show a regular quintet for the CH_3(P) protons (because of strong P-P coupling), indicating a trans arrangement in the cation.[14] Similarly the complexes $\{PtMe[C(OR)CH_2R']L_2\}^+PF_6^-$ (see Table III) for the cases where L = PMe_2Ph show 1:2:1 triplets for the Me(P) protons again confirming a trans configuration. There is evidently free rotation about the Pt-C_{carb} bond in both these classes of compound,[14,88] but restricted rotation about the C_{carb}-N and C_{carb}-O bonds is evident. Nevertheless, the latter compounds do show a long-range coupling ^4J(Pt-C-O-C-H_2R) of ~7 Hz; that analogous couplings have not been observed with ^{183}W is attributed to the greater gyromagnetic ratio of the ^{195}Pt nucleus (see section V.C).

2. Restricted Rotation and Cis and Trans Isomerism

The high double-bond character of the C_{carb}–heteroatom bond of carbene complexes and associated restricted rotation about this bond have been the subject of much spectroscopic investigation. For derivatives of the group VI metal carbonyls, cis-trans isomerism about C_{carb}-X (where X represents the heteroatom) has been demonstrated, particularly for the cases where X = O and N, and the barriers appear to be considerably higher than in carboxylic ester or amides.

The complex **29**, in which ^{14}N (I = 1, quadrupole) has been replaced with ^{15}N (I = $^1/_2$), shows an ABM_3X-type ^{1}H spectrum, clearly showing the double-bond character in the C_{carb}-N bond.[121] Similarly the ^{1}H nmr spectrum of **30** exhibits three methyl signals, those of (N)Me trans, (N)Me cis, and (C)Me.[121] Assignments were simplified by comparison with the diethylamino analog, in which τ values for the (N)-CH_2-groups are very close to those of (N)Me in **30**. The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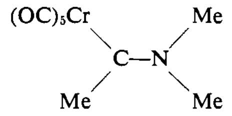
30

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[120] J. Müller and J. A. Connor, *Chem. Ber.*, 102, 1148 (1969).

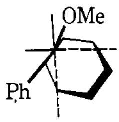
[121] E. Moser and E. O. Fischer, *J. Organometal. Chem.*, 13, 387 (1968); *Naturwissenschaften*, 54, 615 (1967).

aminocarbene complex **30** shows only chemical shift changes at temperatures higher (up to 120°) than the coalescence points of carboxylic acid amides,[122,123] and it has been suggested that the barriers to rotation are therefore higher in the former case.[121] This is consistent with the observation of homoallylic coupling[121] [^5J(H-C-C-N-C-H); for **30** the values are 0.85 ± 0.1 Hz (trans) and ~0.3 Hz (cis)], which have also been observed in methoxymelthylcarbenechromium complexes.[124]

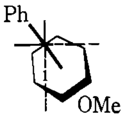
Also interesting is the value of $J(^{15}N\text{-}H)$. Comparison with other values shows that this figure is well in the range observed for sp^2 N atoms.[121] The geminal coupling J(H-N-H) is significantly larger than that in formamide, but the solvent dependence ($|J_{gem}|$ decreases on changing to a solvent of higher dielectric constant) suggests that as in the organic compound J is positive.[121]

The oxycarbene complexes also show restricted rotation,[38,107] but evidently cis and trans isomers are exchanging rapidly (nmr time scale) at room temperature. The two methyl signals found[107] for $(OC)_5CrC(OMe)Me$ at 40° in acetone-d_6 are broadened on cooling.[107] At −40° two pairs of (sharp) signals are seen (at τ 5.11; 7.00 and 5.61, 6.83; former two slightly more intense), the change being fully reversible and each pair corresponding to one of the cis-trans isomeric pair. A comparison of the intensities and line widths shows that J(H-C-O-C-H) is different in the two isomers.[107] A variable-temperature study showed that E_a for the isomerization is 12.4 ± 1.0 kcal/mol (*cf.* 1 kcal/mol in methyl formate[122a]). In perdeuterated acetone and methanol the concentration of isomers is approximately equal; however, in chloro- and fluorobenzene, or deuteriochloroform, the trans form predominates.[107] A more detailed study has been made on the series $(OC)_5CrC(OMe)C_6H_4X$.[38] Coalescence temperatures range from $<-37°$ (X = *p*-Me) to +4° (X = *o*-CF$_3$), activation energies (E_a) from 11.5 (X = *m*-OMe) to 13.8 (X = *p*-Br or *p*-CF$_3$) kcal/mol^{-1}, and preexponential factors (log A) from 12.8 (X = *m*-OMe) to 15.2 (X = *p*-Br); with X = *p*-NMe$_2$ or *p*-OMe, coalescence temperatures are $<-100°$. Steric effects can clearly be more important than electronic: for example, the coalescence temperature for X = OMe is −100° (*p*), but −1.5° (*o*) (with −28° for *m*), and it is not surprising, therefore, that for $(OC)_5CrC(OMe)C_6H_2Me_3$-2,4,6 it is +36°. However, these differences are reflected apparently in log A and not E_a for X = CF$_3$.

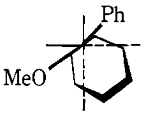
Infrared spectroscopy has revealed another type of hindered rotation in the π-aromatic complex $(\pi\text{-}C_6H_6)(OC)_2CrC(OMe)Ph$ and related species.[125] Various configurations of the molecule, seen along the metal–C$_{carb}$ axis, are shown in **31–34**.



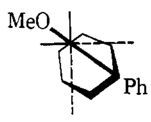
31



32



33

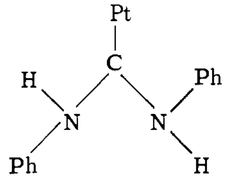


34

These configurations are analogous to those of the pentacarbonyl derivatives where invariably the carbene plane lies approximately at 45° to the (axial) carbonyl substituents (although this type of isomerism does not occur in this series where structures analogous to **31–34** are equivalent). Three types of situation obtain: **31** and **33** (a mirror image pair), **32**, and **34**. Nevertheless, only two pairs of ν(CO) bands are observed, and it may be that one of the situations is sterically unfavorable, although which species are present cannot yet be determined.[125]

In the series $(OC)_4LMC(NHMe)Me$ (L = CO or tertiary phosphine, M = Cr or W) where cis–trans isomers have been distinguished by ^{1}H nmr spectroscopy, the ir spectra show differences of potential stereochemical significance.[63] Thus, in the region 1500–1600 cm^{-1}, the cis derivatives have two absorptions, while the trans analogs have only one, and that at higher wave number (*ca.* 1570 cm^{-1}). There are also distinct differences in the region 600–1000 cm^{-1} between the isomers, although here the presence of phosphine makes interpretation difficult. Ir spectroscopic differences have been observed for $(OC)_5CrC(NHMe)Me$, both in the region 1600–1500 cm^{-1} and in the differing ν(NH) frequencies for cis (3400 cm^{-1}) and trans (3330 cm^{-1}) complexes.[63]

Turning now to the group VIII metal derivatives, evidence of restricted rotation about C$_{carb}$–X bonds has also been obtained, *e.g.*, in the series *trans*-$\{PtX[C(NHR)Q](PEt_3)_2\}ClO_4$ (where Q = PhNH, EtNH, or EtO; and X = Cl or Br).[14] The ^{1}H nmr spectrum (CDCl$_3$) of *trans*-$\{PtCl[C(NHPh)_2](PEt_3)_2\}ClO_4$ shows two different phenyl multiplets, which are not due to spin-spin coupling. In this case it appears that the ligand has the anti configuration **35**. Neither these complexes nor the cationic alkoxycarbenes[88] *trans*-$\{PtMe[C(OR)CH_2R']L_2\}PF_6$ (L = PMe$_2$Ph or AsMe$_3$) show any evidence of restricted rotation about the Pt-C$_{carb}$ bond, although the large coupling [^4J(Pt-C-O-C(R)-H$_2$)] (see above) may be associated with a certain amount of π character in this bond. No homoallylic couplings are observed in the ^{1}H nmr spectra of the fluorophosphate salts (contrast the anti isomers of analogous Cr complexes) which suggests a syn configuration for the carbene ligand.[88]



35

C. ELECTRONIC FACTORS

1. *Nature of the M–C$_{carb}$ Bond for Group VI Metals*

While thermodynamic data are not currently available, there is ample evidence that many metal–carbene compounds have considerable stability. For example, complexes of the group VI metals may be purified by sublimation: some cis platinum complexes described in section III.F melt without decomposition (in one case over 300°), and fragments [metal–carbene]$^+$ generally have high intensities in mass spectra. As seen from section II, the M–C$_{carb}$ bond order in these compounds (judged from metal–C$_{carb}$ bond lengths) is not high, and it was concluded that π-bonding is mainly confined within

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(122) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon, London, 1965, Chapter 8.

(122a) J. P. Lowe, *Progr. Phys. Org. Chem.*, 6, 1 (1968).

(123) T. H. Siddall and W. E. Stewart, *Progr. Nucl. Magn. Resonance Spectrosc.*, 5, 33 (1969).

(124) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, 13, 209 (1968).

(125) H. J. Beck, E. O. Fischer, and C. G. Kreiter, *ibid.*, 26, C41 (1971).

Table IV

^{31}P Nmr Data for Square-Planar Platinum-Carbene Complexes

Compound	*Trans ligand*	*δ, ppm*	*J*(^{195}Pt–^{31}P)	*Ref*
trans-$PtCl_2(PEt_3)_2$	PEt_3	−31.7[f]	2.40[b]	127
trans-$PtCl_2[C(NPhCH_2)_2]PEt_3$[a]	$C(NPhCH_2)_2$	110.8[e]	2.44[c]	90a
trans-$PtCl_2$(*N*-MeBzT)PEt_3[a,g]	*N*-Methylbenzothiazolylidene	107.2[e]	2.44[d]	90a
trans-$PtCl_2[C(NMeCH_2)_2]PEt_3$	$C(NMeCH_2)_2$	110.0[e]	2.35[c]	90a
cis-$PtCl_2[C(NMeCH_2)_2]PEt_3$	Cl	136.2[e]	3.72[c]	90a
cis-$PtCl_2(PEt_3)_2$	Cl	−30.0[f]	3.52[b]	127

[a] The corresponding cis isomer is not soluble. [b] In CH_2Cl_2. [c] In $CHCl_3$. [d] In DMF. [e] Relative to P_4O_6. [f] Relative to 85% H_3PO_4. [g] BzT = benzothiazolylidene.

the carbene ligand. This section describes spectral and other evidence for this proposition, and some of the data have been discussed elsewhere.[5]

One item of evidence relates to ir and nmr shifts for the series (π-C_5H_5)(OC)(ON)MC(OMe)Me compared with (π-C_5H_5)$(CO)_2$(ON)M with lower ν(CO) and ν(NO) and higher $\tau(C_5H_5)$ in the former.[5]

Other data concern electric dipole moments, vibrational force constants, ionization potentials, electronic spectra, and ^{13}C nmr spectra (see section V.C.3).

Dipole moments in cyclohexane have been measured for a number of chromium compounds (Table III). It has been suggested that the high moment of 3.61 D for $(OC)_5CrC(OMe)Me$ implies a strong σ-donor but weak π-acceptor character for the carbene-ligand bond, and variations in moments within the series $(OC)_5CrC(NHY)Me$ (Y = H, 5.64 D; Me, 6.15 D; and C_6H_{11}, 7.17 D) have been cited for further support.[5] We do not find the argument compelling; the parameter required for meaningful discussion would be the M–C_{carb} bond moment, whereas the measurement, of course, provides the molecular moment.

Ir spectra for *n*-hexane solutions of the complexes of formula $(OC)_5CrC(OMe)C_6H_4X$ have provided carbonyl stretching vibrations;[38,125a] their symmetry classes were assigned and Cotton-Kraihanzel force constants k_1–k_3 calculated. There was a reasonably linear relationship between k_1 and the Jaffé σ constant for X = *p*-NMe_2, *p*-OMe, *m*-NMe_2, *p*-Me, H, *p*-F, *p*-Cl, *p*-Br, and *m*-Cl (but less good for *m*-OMe, *m*-CF_3, and *p*-CF_3). Clearly electronic effects are transmitted through the Cr–C_{carb} bond, and as a meta substituent is included, a predominant σ mechanism is indicated. For other Cotton-Kraihanzel force constant calculations on aminocarbene complexes of Cr(0), see ref 125b.

First ionization potentials (IP) for a number of compounds have been recorded from mass spectral data.[38,120] For the series $(OC)_5CrC(NHY)Me$ values range from 6.81 (Y = C_6H_4Me-*p*) to 7.85 eV (Y = $C_6H_4CF_3$-*p*);[120] other data are for $(OC)_5CrC(OMe)C_6H_4Z$ which range from 7.05 (Z = *o*-OMe) to 7.42 eV (Z = *p*-CF_3),[38] $(OC)_5CrC(Q)Me$ (Q = SPh, 7.83; OMe, 7.46; and NH_2, 7.35 eV),[120] and $(OC)_5CrC(NR_2)Me$ (R = Me, 7.15; Et, 7.01 eV).[120] These ionization energies probably relate to loss of an electron from an orbital of principally metal d-orbital character, and electron-withdrawing substituents in the carbene ligand can transmit their electronic effect through the M–C_{carb} bond to cause a relatively higher IP. Consistent with this view, there is a good linear correlation between IP and Hammett σ constants for Z in the series $(OC)_5CrC(NHC_6H_4{\cdot}Z\text{-}p)Me$;[120] it would be of interest to have data for meta Z substituents.

The electronic spectra of a series of compounds $(OC)_5CrC(OMe)C_6H_4{\cdot}X$ and $(OC)_5CrC(OMe)R$ in *n*-C_6H_{14} have been recorded.[38,125a] These generally show a well-defined band in the visible region at 22,000–25,000 cm^{-1} (for Z = NMe_2 or OMe there is an additional band at 28,000 or 32,000 cm^{-1}, respectively) with log ϵ 3.76–4.11 mol^{-1} cm^{-1}. The bands were tentatively assigned to π–π^* transitions, and for limited data a correlation with IP's was suggested for $(OC)_5CrC(Y)Me$: Y = NHMe, ν_{max} 27,400 cm^{-1} and IP = 7.30 eV, compared with (i) 26,500 cm^{-1} and 7.46 eV, for Y = OMe, and (ii) 21,500 cm^{-1} and 7.17 eV, for Y = SPh; we do not find such a correlation self-evident.

2. *Trans Influence in Square-Planar Platinum Complexes*

The trans influence is regarded here as the tendency of a ligand to weaken the bond trans to itself.[126] This problem is now considered for square-planar complexes of Pt(II), for which information on the following is available: (a) metal-halogen stretching frequencies from far-infrared spectra (it is assumed that the frequencies are roughly proportional to the corresponding M–X bond strengths); (b) ^{31}P nmr spectra (it is assumed that there is a correlation between covalency and coupling constants *J*(^{31}P–^{195}Pt) and *J*(^{1}H–^{195}Pt) in the appropriate bonds); (c) metal-ligand bond lengths from structural studies (it is assumed that changes in M–X bond lengths for two complexes differing only in the ligand trans to X is related to the trans influence of that ligand).

Data appropriate for (a), (b), and (c) are in Tables IV–VII. Collectively they suggest that the trans influence of a nucleophilic carbene ligand is similar to that of a trialkylphosphine.

Correlations have also been made between *J*(^1H-Pt) and the trans influence of L in complexes having the trans H-Pt-L and trans Me-Pt-L arrangement. In the series *trans*-$\{PtMe[C(OR)CH_2R']L_2\}^+PF_6^-$, there is evidence for high trans influence of the carbene ligands, here comparable with that of a methyl group.[88] That alkoxycarbenes should show a higher trans influence than amino analogs might be expected from ^{13}C nmr data (see below).

(125a) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Müller, and R. D. Fischer, *J. Organometal. Chem.*, 22, C39 (1970).

(125b) F. T. Delbeke, E. G. Claeys, and C. Van Der Kelen, *ibid.*, 28, 391 (1971).

(126) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(127) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, 6, 1133 (1967).

Table V

Metal–Ligand Stretching Frequencies for Square-Planar Carbene Complexes

Compound	*ν(PtCl₂), cm⁻¹*	*Ref*
trans-$PtCl_2[C(NPhCH_2)_2]PEt_3$	341 s, 326 sh	90a
trans-$PtCl_2[C(NMeCH_2)_2]PEt_3$	339 vs, 326 sh	90a
trans-$PtCl_2$(*N*-MeBzT)PEt_3[a]	347 s, 320 s	90a
trans-$PtCl_2(PEt_3)_2$	340 s	128
trans-$PtCl_2(PPh_3)_2$	345 s	129
cis-$PtCl_2[C(NPhCH_2)_2]PEt_3$	308 s, 277 s	90a
cis-$PtCl_2[C(NMeCH_2)_2]PEt_3$	312 vs, 288 vs	90a
cis-$PtCl_2$(*N*-MeBzT)PEt_3[a]	310 s, 302 sh, 281 s	90a
cis-$PtCl_2[C(OEt)NHPh]PEt_3$	306 s, 284 s	14
cis-$PtCl_2[C(NHPh)_2]PEt_3$	305 s, 278 s	14
cis-$PtCl_2(PEt_3)_2$	303, 281	128

[a] BzT = benzothiazolylidene.

Table VI

Platinum–Phosphorus Bond Lengths in Pt(II) Complexes

Compound	*Trans ligand*	*Pt–P*, Å	*Ref*
trans-$PtCl_2[C(NPhCH_2)_2]PEt_3$	$C(NPhCH_2)_2$	2.29	12, 26
trans-$PtCl_2(PEt_3)_2$	PEt_3	2.30	130
trans-$PtCl(H)(PEtPh_2)_2$	$PEtPh_2$	2.27	131
cis-$PtCl_2[C(OEt)NHPh]PEt_3$	Cl	2.24	114
cis-$PtCl_2(CNPh)PEt_3$	Cl	2.24	114
cis-$PtCl_2(PMe_3)_2$	Cl	2.26 2.24	132

Table VII

Platinum–Chlorine Bond Lengths in Pt(II) Complexes

Compound	*Trans ligand*	*Pt–Cl*, Å	*Ref*
cis-$PtCl_2[C(NPhCH_2)_2]PEt_3$	$C(NPhCH_2)_2$	2.36	26
cis-$PtCl_2[C(NPhCH_2)_2]PEt_3$	PEt_3	2.38	
cis-$PtCl_2[C(OEt)NHPh]PEt_3$	C(OEt)NHPh	2.361	114
cis-$PtCl_2[C(OEt)NHPh]PEt_3$	PEt_3	2.367	
cis-$PtCl_2(PMe_3)_2$	PMe_3	2.36, 2.38	132
trans-$PtCl(H)(PEtPh_2)_2$	H	2.42	131
trans-$PtCl_2(PEt_3)_2$	Cl	2.29	130
cis-$PtCl_2(CNPh)PEt_3$	CNPh	2.33	114

3. ^{13}C *Nmr Spectra*

Modern techniques have made ^{13}C nmr spectra accessible with samples having this isotope in natural abundance.[135,136] For transition metal-carbene complexes the method is potentially of great diagnostic value. Table VIII shows the chemical shifts of the carbene carbon atoms in several chromium complexes and for a platinum compound. The values are similar those found for carbonium ions;[137,138] *e.g.*, the chemical shift of Me_3C^+ is some 273 ppm to lower field than in Me_3CCl.[139] Thus of 18 organometallic compounds examined in ref 23, the carbene $(OC)_5CrC(OMe)Me$ had by far the lowest $\delta(^{13}C)$, although the compound $(\pi\text{-}C_5H_5)(OC)_2FeCOMe$ with the closest δ (^{13}C) has a M–C(sp^2) bond. This is in agreement with our view of coordinated carbenes as electrophilic centers (see section II). This interpretation of the shifts very probably represents a considerable oversimplification; a more appropriate description may require a mixing of electronic states, as has been found for ^{13}C shifts in purely organic systems.[140,141] Nevertheless, the diagnostic value remains and several trends are identifiable. Thus, shifts may be seen to correlate well with the donor–acceptor properties of substituents. The greater degree of C_{carb}–X π-bonding where X = N rather than X = O is reflected in the greater shielding of C_{carb} in aminocarbene complexes. Also noteworthy is an inverse linear relation between $\delta(^{13}C)$ and the wavelength of the electronic charge-transfer band from metal to ligand.

Table VIII

^{13}C C_{carb} Chemical Shifts of Coordinated Carbene Ligands

Compound[a]	*Chemical shift*[b]	*Ref*
Chromium Compounds (Oxycarbene Ligands)		
$(CO)_5CrC(OMe)Me$	362.3	23
$(CO)_5CrC(OMe)Ph$	354.5	133
$(CO)_5CrC(OMe)C_6H_4$-*p*-OMe	342.8	133
$(CO)_5CrC(OMe)C_6H_4$-*p*-Cl	350.1	133
$(CO)_5CrC(OEt)Fc$	332.0	133
$(CO)_5CrC(OEt)Fu$	313.6	133
$(CO)_5CrC(OEt)Th$	319.8	133
Chromium Compounds (Aminocarbene Ligands)		
$(CO)_5CrC(NHMe)Me$	284.8	133
$(CO)_5CrC(NHC_6H_{11})Et$	284.3	133
$(CO)_5CrC(NMe_2)Ph$	277.5	133
$(CO)_5CrC(NC_4H_8)Ph$	271.3	133
$(CO)_5CrC(NC_5H_{10})Ph$	270.5	133
$(CO)_5CrC(NH_2)Fu$	255.6	133
$(CO)_5CrC(NC_4H_8)Fu$	253.7	133
$(CO)_5CrC(NH_2)Th$	271.8	133
Tungsten Compound		
$(CO)_5WC(OMe)Ph$	322.8	133
Platinum Compound		
trans-$Cl_2(Bu^n{}_3P)PtC(NMeCH_2)_2$	196.5	134

[a] Abbreviations: Fc = ferrocenyl, Fu = 2-furoyl, Th = 2-thienyl. [b] Shifts measured relative to Me_4Si in $CDCl_3$, with 10% added C_6F_6. They are ±0.3 ppm.

VI. *Metal–Carbene Complexes as Reaction Intermediates*

Several important organic syntheses may involve carbenes coordinated to a metal center.

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(128) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(129) A. D. Allen and M. C. Baird, *Chem. Ind.* (*London*), 139 (1965).

(130) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).

(131) R. Eisenberg and J. A. Ibers, *ibid.*, **4**, 773 (1965).

(132) G. G. Messmer, E. L. Amma, and J. A. Ibers, *ibid.*, **6**, 725 (1967).

(133) J. A. Connor, E. W. Randall, and E. Rosenberg, unpublished observations.

(134) D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, in press.

(135) E. Breitmeier, G. Jung, and W. Voelter, *Angew. Chem., Int. Ed. Engl.*, 10, 673 (1971).

(136) E. W. Randall, *Chem. Brit.*, 371 (1971).

(137) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

(138) P. S. Pregosin and E. W. Randall, "Physical Methods in Organic Chemistry," Academic Press, New York, N. Y., 1971.

(139) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964.

(140) J. A. Pople, *Discuss. Faraday Soc.*, 34, 7 (1962).

(141) J. A. Pople, *Mol. Phys.*, 7, 301 (1964).

(142) D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Soc. Rev.*, in press.

Table IX

Reactions Involving Complexed Carbene Intermediates

Reactants[a]	*Products*	*Ref*
LMCXY(halogen), alkenes	Cyclopropanes	144, 145
$R^1R^2C(halogen)_2$, Cr^{II}(aq)	Cyclopropanes (etc.)	146
$Ni(CO)_4$, LiR	Acyl compounds	147, 148
$Fe(CO)_5$, LiR	Acyl compounds	149
Strained carbocyclics, various metal catalysts	Valence isomers	150
Diazoalkanes, metal salts (especially Cu^{II})	Carbenes, and subsequent products	151
Olefins (dismutation reaction), metal catalysts	Disproportionated olefins	152

[a] The carbene carbon atom is derived from the reactant on the left-hand side

Some important examples are shown in Table IX, with references. A detailed account of these reactions is given in ref 142; here we briefly describe carbene intermediates in reactions which are not of synthetic value. An example is the cation $\{[(\pi\text{-}C_5H_5)(OC)_2FeCH_2]^+\}$,[72] prepared either from the analogous chloro- or methoxymethyl- compounds. Some evidence for this species is provided by the *stereospecific* trapping of methylene by *cis*- or *trans*-2-butenes and also after separation of other products.[71] Further examples are $\{(Ph_3P)_2(OC)ClIrCH_2\}$, possibly an intermediate in the insertion of CH_2 from CH_2N_2 into the Ir–Cl bond of *trans*-$(Ph_3P)_2(OC)ClIr$,[81] and $\{[(\pi\text{-}C_5H_5)(OC)_3MoCH_2]^+\}$, formed by reaction of silver salts with $(\pi\text{-}C_5H_5)(OC)_3MoCH_2Cl$.[71] A related anion $\{[(\pi\text{-}C_5H_5)(OC)_3MoCH_2]^-\}$ has been postulated as an intermediate (eq 50).[143] The methyl

$$(\pi\text{-}C_5H_5)(OC)_3MoCH_2SiMe_3 + [(\pi\text{-}C_5H_5)(OC)_3Mo]^-Na^+ \longrightarrow \{[(\pi\text{-}C_5H_5)(OC)_3MoCH_2]^-Na^+\} \xrightarrow{\text{solvent}} (\pi\text{-}C_5H_5)(OC)_3MoCH_3 \quad (50)$$

group of the product has been shown by isotopic labeling to be that derived from the CH_2 group of the silylmethyl species. The unusually reactive C–Si bond is presumably related to a large neighboring-group effect stabilization in the methylene-molybdenum anion.

Acknowledgments. The authors thank J. A. Connor, A. W. Johnson, E. W. Randall, and D. Seyferth for unpublished information.

VII. Addendum

This section, added in proof, provides a brief account of material published since the submission of the manuscript, and makes possible coverage of the literature up to August 1972. The text reports new developments, and Tables X and XI (which appear in the microfilm edition) provide structures and molecular parameters[166–172] and data,[173–192] respectively, on new compounds. Recent work from Fischer's laboratory has been summarized in two short reviews.[153,154]

^{13}C nmr spectra confirm that the carbene carbon atom is highly deshielded in a series of Cr and W complexes[155] and for a Pt compound.[156] The electrophilic character of the carbene center is further illustrated by the chemical shifts of the α protons in secondary (CHX) carbenes [for Cr, Fe, Rh, -1.2 to $+0.9$ ($CDCl_3$)].[157]

Experimental details are now available for the series of cationic carbene complexes of platinum reported briefly in ref 88a (see Table III).[158] Carbenes derived from the Cr group metal complexes have been trapped both by Ph_2SiH_2[159] and by olefins with cyclopropane formation.[160] Electron-rich olefins have been shown to react with both $Fe(CO)_5$ and $Cr(CO)_6$ affording mono- and dicarbene complexes, respectively;[161] details are now available for the carbene transfer reactions from $(\pi\text{-}C_5H_5)(OC)(ON)MoC(X)Ph$ to $Fe(CO)_5$,[162] and it is possible that these proceed *via* the intermediate electron-rich olefins Ph(X)C=C(X)Ph. Differing orientations of the naphthyl group in $(OC)_5CrC(NHCHMePh)$-1-naphthyl give rise to isomerism of a type not previously known in carbene complexes.[163] Trialkylphosphines, -arsines, and -stibines react with $(OC)_5CrC(OMe)Me$ in benzene to yield cis–trans mixtures of the substituted products, whereas the triaryl analogs afforded only the cis isomers.[164] The secondary phosphine $PHMe_2$ by contrast affords an adduct $(OC)_5CrC(OMe)(Ph)PHMe_2$ with the methoxyphenylcarbene complex, and carbon monoxide is not displaced.[165] The porphine complexes **5** and **6** have now been reformulated without carbene ligands.[165a]

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(143) M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Commun.*, 1498 (1970).

(144) M. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964).

(145) D. Seyferth, *Accounts Chem. Res.*, **5**, 65 (1972).

(146) C. E. Castro and W. C. Kray, Jr., *J. Amer. Chem. Soc.*, **88**, 4447 (1966).

(147) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183 (1970).

(148) M. Ryang, K.-M. Song, Y. Sawa, and S. Tsutsumi, *J. Organometal. Chem.*, **5**, 305 (1966).

(149) Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).

(150) M. Sakai, H. H. Westburg, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **93**, 4611 (1971); P. G. Gassman and T. Nakai, *ibid.*, **93**, 5897 (1971); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971).

(151) W. R. Moser, *ibid.*, **91**, 1135, 1141 (1969).

(152) D. J. Cardin, M. J. Doyle, and M. F. Lappert, *Chem. Commun.*, 927 (1972).

(152a) Tables X and XI will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number CR-72-545. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(153) C. G. Kreiter and E. O. Fischer, *Pure Appl. Chem., Suppl.*, **6**, 151 (1971).

(154) E. O. Fischer, *Rev. Pure Appl. Chem.*, **30**, 353 (1972).

(155) C. G. Kreiter and V. Formaček, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972).

(156) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).

(157) B. Çetinkaya, M. F. Lappert, and K. Turner, *ibid.*, 851 (1972).

(158) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **11**, 503 (1972).

(159) E. O. Fischer and K. H. Dötz, *J. Organometal. Chem.*, **36**, C4 (1972).

(160) K. H. Dötz and E. O. Fischer, *Chem. Ber.*, **105**, 1356 (1972).

(161) B. Çetinkaya and M. F. Lappert, to be published.

(162) E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Müller, and E. Winkler, *Chem. Ber.*, **105**, 162 (1972).

(163) H. Brunner, E. O. Fischer, and M. Lappus, *Angew. Chem., Int. Ed. Engl.*, **10**, 924 (1971).

(164) E. O. Fischer. H. Fischer, and H. Werner, *ibid.*, **11**, 644 (1972).

(165) F. R. Kreissl, C. G. Kreiter, and E. O. Fischer, *ibid.*, **11**, **643** (1972).

(165a) A. W. Johnson and A. L. Hamiltor, personal communication.

(166) E. O. Fischer, E. Winkler, C. G. Kreiter, G. Huttner, and B. Kreig, *ibid.*, **10**, 922 (1971).

(167) R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 653 (1972).

(168) C. K. Prout, T. S. Cameron, and A. R. Gent, *Acta Crystallogr., Sect. B*, 28, 32 (1972).

(169) G. Huttner and D. Regler, *Chem. Ber.*, **105**, 2726 (1972).

(170) E. O. Fischer, E. Winkler, G. Huttner, and D. Regler, *Angew. Chem., Int. Ed. Engl.*, **11**, 238 (1972).

(171) G. Huttner and W. Gartzke, *Chem. Ber.*, **105**, 2714 (1972).

(172) J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **93**, 4613 (1971).

(173) E. O. Fischer and F. R. Kreissl, *J. Organometal. Chem.*, **35**, C47 (1972).

(174) E. O. Fischer, M. Leupold, C. G. Kreiter, and J. Müller, *Chem. Ber.*, **105**, 150 (1972).

(175) E. O. Fischer and H. J. Beck, *ibid.*, 104, 3101 (1971).

(176) E. O. Fischer and M. Leupold, *ibid.*, **105**, 599 (1972).

(177) E. O. Fischer and S. Fontana, *J. Organometal. Chem.*, **40**, 367 (1972).

(178) E. O. Fischer and S. Fontana, *ibid.*, 40, 159 (1972).

(179) E. O. Fischer, F. R. Kreissl, C. G. Kreiter, and E. W. Meineke, *Chem. Ber.*, 105, 2558 (1972).

(180) J. A. Connor and J. P. Lloyd, *J. Chem. Soc., Dalton Trans.*, 1470 (1972).

(181) C. W. Rees and E. Angerer, *Chem. Commun.*, 420 (1972).

(182) P. M. Treichel, J. P. Stenson, and J. J. Benedict, *Inorg. Chem.*, **10**, 1183 (1971).

(183) E. O. Fischer, F. R. Kreissl, and E. Winkler, *Chem. Ber.*, **105**, 588 (1972).

(184) K. Öfele and C. G. Kreiter, *ibid.*, **105**, 529 (1972).

(185) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, 94, 4354 (1972).

(186) P. G. Mente and C. W. Rees, *Chem. Commun.*, 418 (1972).

(187) P. R. Branson and M. Green, *J. Chem. Soc., Dalton Trans.*, 1303 (1972).

(188) G. A. Larkin, R. P. Scott, and M. G. H. Wallbridge, *J. Organometal. Chem.*, 37, C21 (1972).

(189) A. L. Balch, *ibid.*. 37, C19 (1972).

(190) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 1484 (1971); *J. Amer. Chem. Soc.*, 94, 1532 (1972).

(191) B. Çetinkaya, P. Dixneuf, and M. F. Lappert, to be published.

(192) F. Bonati and G. Minghetti, *Syn. Inorg. Metal-Org. Chem.*. **1**, 299 (1971).